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Inspection Manual for the Enforcement of New Source Performance Standards as Applied to Contact Catalyst Sulfuric Acid Plants

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Prepared for

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SULFURIC ACID PLANTS

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Standards of performance for new sulfuric acid plants were promulgated under Section 111 of the Clean Air Act on December 16, 1971; the standards have been subjected to several amendments since that time. This report presents procedures for inspection of Contact Catalyst Sulfuric Acid Plants toward determination of their compliance with NSPS. It also includes background information that will aid the inspector in understanding the manufacture of sulfuric acid using the Contact Catalyst process. The report provides a list and description of the critical process controls related to major operating parameters of the process.

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INSPECTION MANUAL FOR THE ENFORCEMENT OF NEW SOURCE PERFORMANCE STANDARDS

AS APPLIED TO CONTACT CATALYST SULFURIC ACID PLANTS

by

E. L. Calvin
F. D. Kodras

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November 1976

EPA PROJECT OFFICER: Donald F. Carey

Prepared For

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EPA REVIEW NOTICE

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ABSTRACT

This report describes an inspection manual designed to aid air pollution control officials in enforcing New Source Performance Standards (NSPS) as applied to sulfuric acid plants:

This manual includes:

1. A brief description of the processes involved including flow diagrams with the points of emissions indicated.
2. A checklist of inspection points for process and air pollution control equipment where emissions may occur.
3. Detailed information about the emission points for each process and the control equipment at these points, including diagrams, in order that an inspector can more readily identify such emission points and determine if emissions are exceeding applicable NSPS.
4. A list and description of the operation of the critical process control and monitoring instrumentation - pressure gages, flow meter, etc. - which an inspector should examine to determine process rate, emissions, and maintenance of such equipment.
5. A checklist and inspection log to be carried by the inspector for each operation.
6. A set of recommended records and/or recordkeeping procedures which the operator may require to be adopted so that enforcement personnel may assess past activities and ascertain if the operator has maintained compliance with the regulations.

7. Detailed information about deviations in the normal process operating parameters which temporarily result in exceeding the emission standards during startups, shutdowns and malfunctions and measures which can be taken to minimize emissions in such events.

8. Detailed information on the operating parameters for each source which should be observed prior to or during the conducting of performance tests.

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SECTION 1

INTRODUCTION

Federal New Source Performance Standards have been promulgated by EPA for new sulfuric acid plants. To ensure consistent and uniform implementation and enforcement of these standards, standardized procedures must be developed for engineering inspection of new sources to determine compliance with the NSPS requirements. The purpose of this manual is (1) to examine the chemical processes and control systems likely to be incorporated into a modern sulfuric acid plant, (2) to determine operation and maintenance practices, and (3) to determine conditions which might affect the ability of the source to meet the prescribed emission standards. This information is incorporated into this technical guide for field inspection of new sources.

Under Section 111 of the Clean Air Act (42U.S.C.1857 et. seq.) as amended by the Clean Air Amendments of 1970 (Public Law 91-604), the Administrator of the EPA is authorized to develop and promulgate standards of performance for new stationary sources.

The standards of performance for new sulfuric acid plants were promulgated on December 16, 1971, and were published in the Federal Register on December 23, 1971. Since that time these standards have been subject to several amendments.

Each state may develop a program for enforcing NSPS applicable to sources within its boundaries. If this program is adequate, EPA will delegate implementation and enforcement authority to the state for all affected sources with the exception of those owned by the U.S. Government. Coordination of activities between the state agency and the EPA, both Regional Office and Division of Stationary Source Enforcement, is essential for effective operation of the NSPS program. To facilitate state participation, EPA has established guidelines identifying the administrative procedures the states should adopt to effectively implement and enforce the NSPS program.

The long-term success of the NSPS program depends essentially upon the adoption of an effective plant inspection program. Primary functions of the inspection program are monitoring the NSPS performance tests and routine field surveillance. This manual provides guidelines for conducting such field inspections. The basic inspection procedures presented in this manual should be of use in enforcing emission regulations contained in state air quality implementation plans.

SECTION 2 - The New Source Performance Standards and the state emission standards that sulfuric acid plants must meet are reviewed and summarized. This inspection manual is designed to aid air pollution control officials in enforcing New Source Performances Standards as applied to sulfuric acid plants.

SECTION 3 - This manual includes (1) a brief description of the processes, including flow diagrams with the points of emissions indicated, (2) a checklist of inspection points for process and air pollution control equipment, and (3) detailed information about the emission points for each process and the control equipment at these points, including diagrams, in order that an inspector can more readily identify emission points and determine if emissions are exceeding applicable NSPS.

SECTION 4 - Includes a set of recommended records and/or recordkeeping procedures the operator may be required to adopt so that enforcement personnel may assess past activities and ascertain if the operator has maintained compliance with the regulations. A list and description is given of the operation of the critical process control and monitoring instrumentation - pressure gages, flow meter, etc. - which an inspector should examine to determine process rate, emissions, and maintenance of such equipment.

SECTION 5 - Detailed information about deviations in the normal process operating parameters which temporarily result in exceeding the emission standards during startups, shutdowns, and malfunctions and measures which can be taken to minimize emissions in such events are outlined.

SECTION 6 - Contains detailed information on the operating parameters for each source which should be observed prior to or during the conducting of performance tests.

SECTION 7 - Consists of a checklist and inspection log for each operation to be carried out by the inspector.

SECTION 2

STATE IMPLEMENTATION PLANS (SIP) AND NEW SOURCE PERFORMANCE STANDARDS (NSPS)

State Implementation Plans (SIP) regulations applicable to sulfuric acid plants are summarized in Table 1.

Sulfuric acid production facilities can discharge sulfur dioxide as well as acid mist and nitrogen oxides. At this time, standards of performance are established only for sulfur dioxide, acid mist and for attendant visible emissions which are a function of acid mist. The latter pollutant is a "non-criteria pollutant" as defined by Section 111(d) of the Act, and requires the establishment of state emission standards for existing sources.

SUMMARY OF NEW SOURCE PERFORMANCE STANDARDS (NSPS)

Emission Standards

Sulfur Dioxide Standard -

"(a) On and after the date on which the performance test required to be conducted by 60.8 is completed, no owner or operator subject to the provisions of this subpart shall cause to be discharged into the atmosphere from any affected facility any gases which contain sulfur dioxide in excess of 2 kg per metric ton of acid produced (4 lb. per ton), the production being expressed as 100 percent H_2SO_4." (39 FR 20790, June 14, 1974).

Acid Mist Standard -

"(a) On and after the date on which the performance test required to be conducted by 60.8 is completed, no owner or operator subject to the provisions of this subpart shall cause to be discharged into the atmosphere from any affected facility any gases which: (1) Contain acid mist, expressed as H_2SO_4, in excess of 0.075 kg per metric ton of acid produced (0.15 lb. per ton), the production being expressed as 100 percent H_2SO_4. (2) Exhibit 10 percent opacity, or greater. Where the presence of uncombined water is the only reason for failure to meet the requirements of this paragraph, such failure will not be a violation of this section." (39 FR 20790, June 14, 1974).

EMISSION LIMITATION SUMMARIES

Table 1

REGULATIONS APPLICABLE TO STATED SOURCES

	Sulfuric Acid Plants	
	Mist	SO_2
	Lbs/Ton 100% Acid	Lbs SO_2/Ton 100% Acid
ALABAMA	0.5[13]	6.5
ALASKA		
ARIZONA		
ARKANSAS[30]		
CALIFORNIA[2]		
COLORADO[1]		
CONNECTICUT		6.5
DELAWARE		__[3]
DIST. OF COL.		
FLORIDA	0.15[4]	4.0[5]
GEORGIA	0.15	4.0
HAWAII		
IDAHO		
ILLINOIS	0.15	4.0[6]
INDIANA[6]		
IOWA	0.5[8]	30.0[8]
KANSAS	0.5[9]	30.0[9]
KENTUCKY	0.15[10]	4.0[11]
LOUISIANA		6.5
MAINE		
MARYLAND[31]		
MASSACHUSETTS		4.0[12]
MICHIGAN[13]	0.7	6.5
MINNESOTA	.15[28]	4.0[29]
MISSISSIPPI	0.5	
MONTANA		
NEBRASKA		
NEW HAMPSHIRE	__[32]	
NEW JERSEY[37]		
NEW MEXICO	__[16]	2.0[17]
NEW YORK	0.15	4.0
NORTH CAROLINA	0.5	27.0
OHIO	0.5	6.5
OKLAHOMA[34]	0.15	4.0
OREGON		
PENNSYLVANIA	0.5	6.5
SOUTH CAROLINA	0.5	10.0[19]
SOUTH DAKOTA	__[33]	__[33]

Table 1 (continued)

	Sulfuric Acid Plants	
	Mist	SO_2
	Lbs/Ton 100% Acid	Lbs SO_2/Ton 100% Acid
TENNESSEE	0.5[20]	6.5[21]
TEXAS		—[22]
UTAH	—[34]	—[34]
VERMONT		
VIRGINIA	—[23]	27.0[24]
WASHINGTON	—[25]	—[25]
WEST VIRGINIA[26]		30.0[27]
WISCONSIN		4.0
WYOMING	0.15	4.0
AMERICA SAMOA		
GUAM		
PUERTO RICO	—[38]	6.5
VIRGIN ISLANDS		

Table I - Footnotes

[1] Only ground level standards given.

[2] Each county has its own regulations.

[3] 1000 ppm by volume for existing plants; 500 ppm by volume for new plants.

[4] For new plants only; no regulations stated for existing plants.

[5] For plants constructed after January 1, 1972; 10 lbs SO_2 ton 100% acid for plants constructed before January 1, 1972.

[6] For new plants only; no regulation given for existing sulfuric acid plants.

[7] East Chicago: Sulfuric Acid Plants - 6.5 lbs SO_2/ton 100% acid; 0.5 lbs/ton 100% acid.

[8] After January 1, 1974 for mist; after January 1, 1975 for SO_2.

[9] Per ton of 98% acid.

[10] For new plants only; 0.9 lb/ton 100% acid for existing plants.

[11] For new plants only; 27.0 lbs SO_2/ton 100% acid for existing plants.

[12] For all AQCR's, for new plants only; 27.0 lbs SO_2/ton 100% acid for existing sulfuric acid plants.

Table I - Footnotes (continued)

[13] These regulations are for Wayne County; no regulations were stated for the state.

[14] For new plants only; 1.7 lbs/ton 100% acid for existing plants.

[15] For new plants only; 6.5 lbs SO_2/ton 100% acid for existing plants.

[16] See paragraph 4704.40.

[17] For new plants only; for existing sources after December 31, 1972:

Tons/day capacity	lbs. SO2/100 lbs. SO_2	Type plant
200	5.0	All acid plants except those manufacturing sulfuric acid from H_2S gas.
200	7.0	Acid plants manufacturing sulfuric acid from H_2S gas.
200	3.0	Sulfuric acid plant.

[18] lbs SO_2/100 lbs SO_2 for new plants only, no regulations stated for existing plants.

[19] 4.0 lbs SO_2/ton 100% acid by July 1, 1977.

[20] After July 1, 1975; until July 1, 1975, 0.15 lb/ton.

[21] After July 1, 1975; until July 1, 1975, 4.0 lbs SO_2/ton.

[22] 34.7 lbs SO_2/hr/1000 scfm effluent flow rate for plants burning other than elemental sulfur; 19.8 lbs SO_2/hr/1000 scfm effluent flow rate for plants burning elemental sulfur.

[23] All plants must reduce acid mist emissions to not more than 5.0 mg. H_2SO_4 including uncombined SO_2 per standard cubic foot.

[24] When elemental sulfur is used; 45 lbs SO_2/ton 100% acid when other materials are used as feed.

[25] Northwest APA: Sulfuric acid plants--20 lbs SO_2/ton 100% acid.

[26] By June 30, 1975.

Table I - Footnotes (continued)

[27] When elemental sulfur is used; 40 lbs SO_2/ton 100% acid when other materials are used as feed.

[28] For new or modified plants only.

[29] Sulfur trioxide emissions not to exceed 0.2 lb SO_2/ton.

[30] Sulfur Dioxide....................................
Sulfuric acid mists or sulfur trioxide.............
0.20 parts per million
30.0 micrograms per cubic meter

[31] For all 6 AQCRS.

[32] 35 milligrams/dry cubic meter at standard conditions.

[33] The Commission may establish emission limitations if it is determined that any source is causing ambient air quality standards to be exceeded.

[34] All new installations with a potential for emission of sulfur oxides in an amount greater than 250 tons of sulfur per year as a gaseous or mist effluent, shall install such controls as are necessary to result in discharge to the atmosphere of 20% or less of input sulfur to the effluent sulfur removal device.

[35] Sulfur dioxide in tail gases from existing sulfur recovery operations shall not exceed a concentration of 8000 ppm by volume and shall not exceed a mass emission rate of:

Sulfur Production Rate (tons/day)	SO_2 Mass Emission Rate (lbs/hr)
50	415
100	830
200	1660
300	2490
400	3320
500	4150

[36] For plants constructed after April 3, 1972; 5.5 lbs/ton after July 1, 1975.

[37] Maximum SO_2 concentration from a stack is limited to 2000 ppm. Quantitative allowable emission rate for sulfur compounds in the form of gases, vapors, or liquid particles is a function of stack height and velocity and temperature of gases through the stack.

[38] No regulations for acid mist.

Performance Testing

Compliance with the NSPS is determined only by performance tests of 60.8 conducted by the operator to furnish a written report of the tests. The arithmetic mean of three test runs will be used to determine compliance with the NSPS. The operating conditions for the performance tests are to be representative of normal plant performance. The test conditions will be determined from records furnished by the operator. The operator is to provide the following performance testing facilities:

1. Adequate sampling ports.
2. Safe sampling platforms.
3. Safe access to sampling platforms.
4. Utilities for sampling and testing equipment.

Performance tests are to be made within 60 days of achieving the maximum production rate, but no longer than 180 days after startup. Thirty days' notice must be given to the EPA.

Stack and Process Monitoring

Sulfuric acid plant operations are to install, operate, calibrate, and maintain an instrument to continuously monitor and record sulfur dioxide emissions. The instrument and sampling system is to be capable of providing a measurement of emission concentration within ± 20 percent with a 95 percent confidence level. The instrument is to be calibrated using manufacturer's prescribed methods. The manufacturer's recommended zero adjustments and calibrations are to be made once every 24 hours or more often if recommended by the manufacturer.

Recordkeeping and Reporting

All records are to be kept by the plant for two years following the date of measurement and summary. Performance records must be made available to EPA. Emission data shall be made available to the public. Table 2 summarizes the items to be recorded and the frequency of data to be recorded.

The promulgation of the September 11, 1974 additions will revise the recordkeeping and reporting requirements. Data reduction will be performed monthly rather than daily, allowing the use of computerized data reduction techniques.

Sulfuric acid plant production rate and hours of operation are to be recorded daily.

A written report of excess emissions must be filed by the operator for each calendar quarter. The report is due by the thirtieth day following the end of the quarter and is required only if excess emissions occurred. The report shall include:

1. Magnitude of excess emissions by monitoring equipment reduced to units of the standard.
2. Date of excess emissions.
3. Time excess emissions started.
4. Time excess emissions were corrected.
5. Identify cause of excess emissions such as startup, shutdown, or malfunction.
6. Nature and cause of any malfunction.

7. Corrective action taken to correct malfunction.

8. Measures adopted to prevent reoccurrence.

Emissions occurring two or more consecutive hours with average sulfur dioxide concentration exceeding four pounds per ton of acid produced must be reported. (Refer to Section 5)

APPLICABILITY OF STANDARDS

These performance standards shall apply to contact process sulfuric acid and oleum facilities that burn elemental sulfur, alkylation acid, hydrogen sulfide, organic sulfides, mercaptans, or acid sludge. They do not apply to metallurgical plants that use acid plants as SO_2 control systems, or to chamber process plants or acid concentrators.

Table 2

RECORDKEEPING REQUIREMENTS FOR SULFURIC ACID PLANTS

Item	Applicable to Burning Sulfur	Recordkeeping Frequency	Comments*
Plume from state exit	All[a]	Continuous	Convert to opacity.
SO_2	All	Continuous	Convert to lb/MM Btu, required for use of low-sulfur fuel.
Acid Mist	All	Continuous	Convert to lb.
Production rate - Sulfuric Acid, 100%	All	Daily	Daily hours of production.
Compliance tests	All	As required	
Instrumentation calibration	All	As required	
Malfunctions, startup shutdowns, etc.	All	As required[b]	

[a] Contact process burning elemental sulfur, alkylation acid, hydrogen sulfide, organic sulfides, mercaptans, or acid sludge, but does not include pyritic ores, smelters and roaster cleanup.

[b] Revised Federal Register, Vol. 38, No. 84, May 2, 1973. Quarterly reports are required including malfunction, corrective actions and preventive means.

* Refer to Appendix "A".

SECTION 3

PROCESS DESCRIPTION, ATMOSPHERIC EMISSIONS, AND EMISSION CONTROL METHODS

PROCESS DESCRIPTION

Contact Sulfuric Acid Process

Although variations occur in feed or application, all contact acid plants contain the same five operations.

1. Burning sulfur or sulfur bearing feeds to produce sulfur dioxide.
2. Cooling the dilute sulfur dioxide gas.
3. Catalytic oxidation of the sulfur dioxide to sulfur trioxide.
4. Cooling the oxidized gas containing sulfur trioxide.
5. Absorbing sulfur trioxide in strong sulfuric acid.

The simplest contact plant configuration uses elemental sulfur as feed. When acid or acid sludge feeds are used, additional processing steps must be added to remove water and particulate matter before processing the combustion products in the catalytic converter. Plant feed variations will affect the sulfur conversion ratio, the volume of exhaust gases, and the character and amount of pollution emitted. The processes discussed will use elemental sulfur as feed. References (1), (2), (3), and (4) outline detailed process descriptions for additional acid plant background information.

Single Absorption Process

A simplified process flow diagram for a single absorption contact sulfuric acid plant burning elemental sulfur is presented in Figure 1.

Cooling Sulfur Trioxide Gas

The gas leaving the converter heats boiler feed water in an economizer before going to the acid absorber.

Absorbing Sulfur Trioxide

The final sulfuric acid product is manufactured by passing the gases through an absorption tower. Product acid strengths can be varied by controlling the water makeup to the acid circulating system. Absorption efficiency is affected by the temperature of the absorbing acid.

If fuming sulfuric acid or oleum is required, a portion of the gases containing sulfur trioxide leaving the economizer are passed through oleum towers where sulfur trioxide is absorbed in re-circulated oleum with makeup 98.5 percent acid.

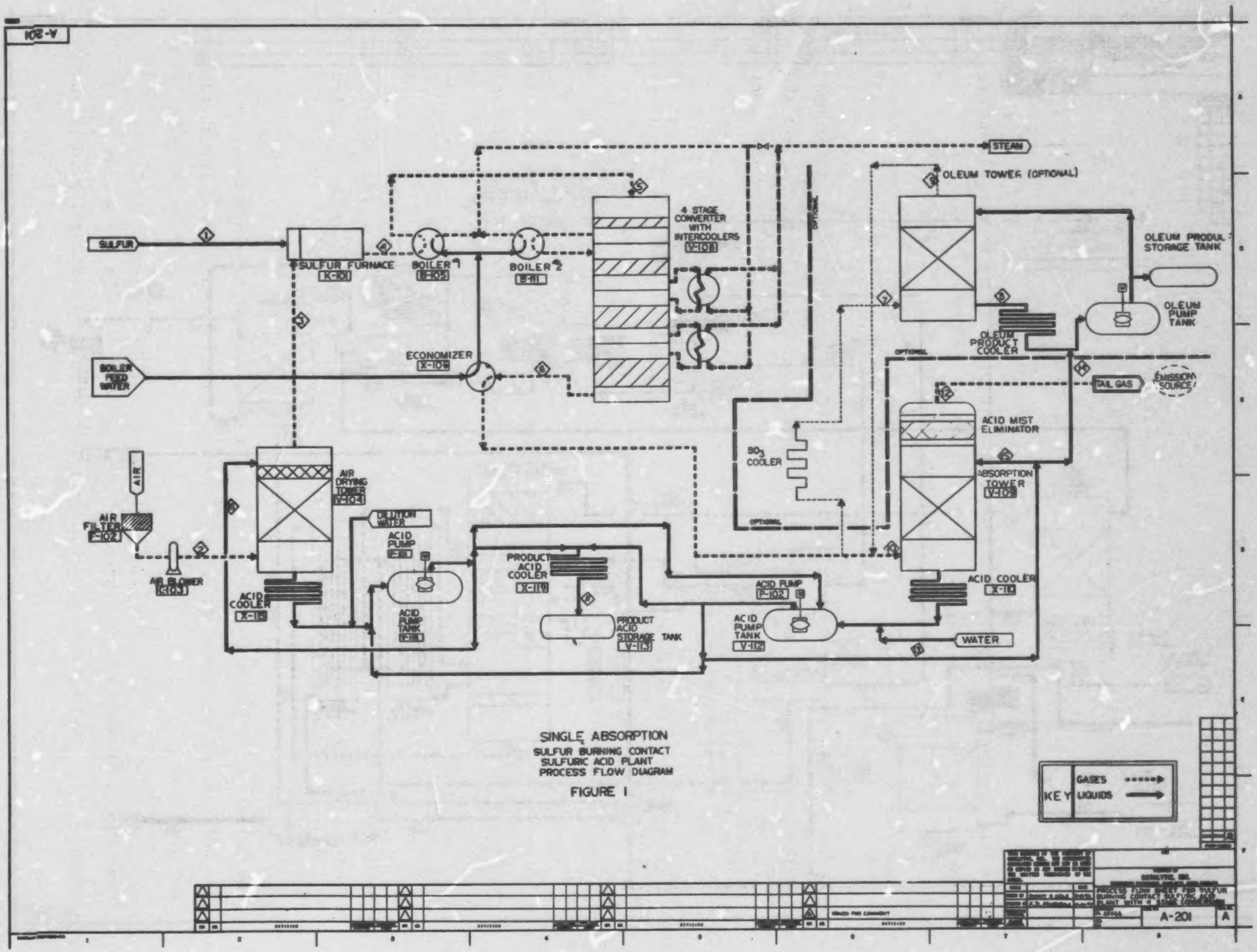
The gas stream leaving the oleum tower is stripped of sulfur trioxide by passing through a standard acid absorber containing 98.5 to 98.8 percent sulfuric acid.

Dual Absorption Processes

An example of a typical modern dual absorption plant is shown in Figure 2. Such a plant can convert 99.7 to 99.8 percent of the sulfur dioixde to sulfur trioxide.

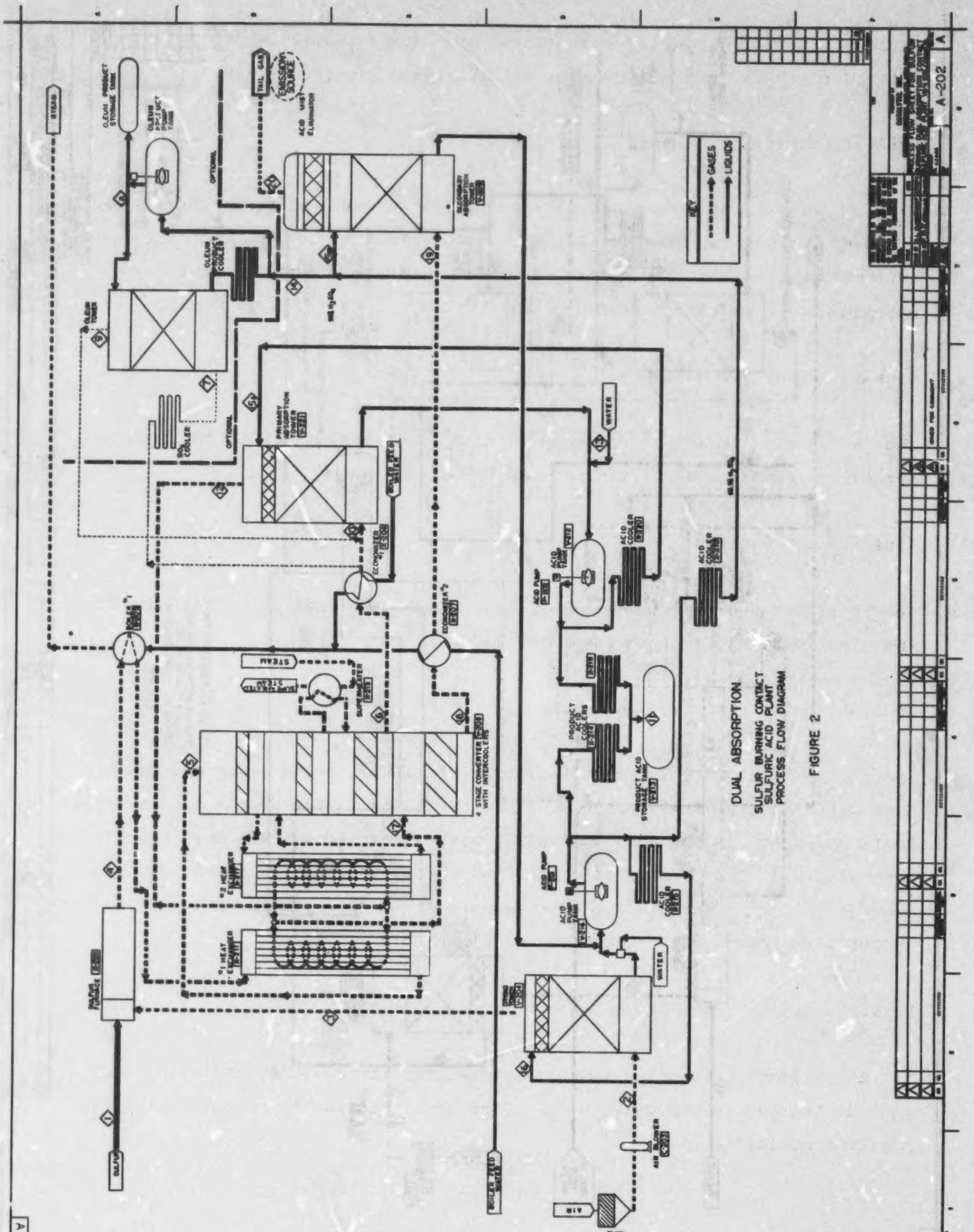
The primary difference between the single and dual absorption processes is the addition of a primary sulfur trioxide absorber for gas leaving the third catalyst bed.

Some processes use this absorber after the second bed. The gas stream is cooled before this interstage absorber and is reheated before going to the next


A-201
SULFUR
1
SULFUR FURNACE
K-101
2
3
4
BOILER 1
B-105
BOILER 2
B-111
5
4 STAGE CONVERTER WITH INTERCOOLERS
V-108
6
ECONOMIZER
X-106
BOILER FEED WATER
AIR
AIR FILTER
F-102
AIR BLOWER
C-103
AIR DRYING TOWER
V-104
ACID COOLER
X-115
DILUTION WATER
ACID PUMP
ACID PUMP TANK
PRODUCT ACID COOLER
X-119
8
PRODUCT ACID STORAGE TANK
V-113
ACID PUMP
P-102
ACID PUMP TANK
V-112
WATER
13
STEAM
OPTIONAL
SO_3 COOLER
OPTIONAL
OPTIONAL
7
9
OLEUM TOWER (OPTIONAL)
OLEUM PRODUCT COOLER
OLEUM PRODUCT STORAGE TANK
OLEUM PUMP TANK
14
TAIL GAS
EMISSION SOURCE
12
ACID MIST ELIMINATOR
15
ABSORPTION TOWER
V-109
10
ACID COOLER
X-110
KEY
GASES
LIQUIDS
PROCESS FLOW SHEET FOR SULFUR BURNING CONTACT SULFURIC ACID PLANT WITH 4 STAGE CONVERTER
A-201
A

SINGLE ABSORPTION
SULFUR BURNING CONTACT
SULFURIC ACID PLANT
PROCESS FLOW DIAGRAM

FIGURE 1


SULFUR
SULFUR FURNACE
STEAM
BOILER
BOILER FEED WATER
AIR
AIR FILTER
AIR BLOWER
DRYING TOWER
WATER
ACID PUMP TANK
ACID PUMP
ACID COOLER
PRODUCT ACID COOLERS
PRODUCT ACID STORAGE TANK
#1 HEAT EXCHANGER
#2 HEAT EXCHANGER
4 STAGE CONVERTER WITH INTERCOOLERS
SUPERHEATER
SUPERHEATED STEAM
ECONOMIZER #1
ECONOMIZER #2
PRIMARY ABSORPTION TOWER
SO3 COOLER
OPTIONAL
OLEUM TOWER
OLEUM COOLER
OLEUM PRODUCT PUMP TANK
OLEUM PRODUCT STORAGE TANK
SECONDARY ABSORPTION TOWER
ACID MIST ELIMINATOR
TAIL GAS
EMISSION SOURCE
KEY
GASES
LIQUIDS
A-202
A

DUAL ABSORPTION

SULFUR BURNING CONTACT
SULFURIC ACID PLANT
PROCESS FLOW DIAGRAM

FIGURE 2

catalyst bed. The type and arrangement of heat exchangers varies, but this cooling and reheating operation is included in all designs.

Sulfur Burning

The sulfur combustion portions of the single and dual absorption plants are similar. Combustion air is dried in a tower with 93 to 98 percent sulfuric acid before being introduced in the sulfur furnace. Furnaces normally operate with gas strengths of 9-12 percent SO_2.

Cooling Sulfur Dioxide Gas

The waste heat boiler is designed to permit the cooling of the gas to the required converter inlet temperature of 795-820°F.

Catalytic Oxidation

The cooled gases pass through the first bed of the catalytic converter where the gas temperature is increased to 1100-1130°F.

Cooling Sulfur Trioxide Gas

The high temperature gas leaving the first catalyst stage is cooled in the No. 2 heat exchanger to about 820°F for reaction in the second catalyst bed. Heat generated in the second catalyst bed is removed by the waste heat boiler superheater. Heat generated in the third catalyst bed is removed by an economizer in the boiler feed water system. The cool gas flows to the primary absorption tower after the third catalyst bed.

Primary Sulfur Trioxide Absorbing

In the primary absorption tower the concentration of sulfur trioxide in the gas is reduced to approximately 100 parts per million by contact with 98.5 percent sulfuric acid.

Gas Reheating

The cold gas leaving the primary absorption tower must be reheated by passing in parallel through No. 1 and No. 2 heat exchangers before introduction to the fourth catalyst bed.

Catalytic Oxidation

Approximately 97 percent of the sulfur dioxide remaining in the gas stream is converted to sulfur trioxide in the fourth catalyst bed. A higher overall conversion rate than is possible in a single absorption plant and lower partial pressure of sulfur trioxide drive the reaction with increased conversion efficiency.

Secondary Sulfur Trioxide Absorption

The gases leaving the fourth catalyst bed are cooled in a second economizer while also heating boiler feed water. The cooled gas passes to a secondary absorption tower containing 98.5 percent sulfuric acid. The gases leaving the secondary absorption tower will contain about 100 to 300 parts per million sulfur dioxide and will meet the existing emission standards without further processing.

If required, an oleum tower is installed before the primary absorber and is similar to the single absorption process.

With the exception of the primary absorber and arrangement of the heat exchangers, all major designs of dual absorption sulfuric plants use similar equipment configurations. Design variations are found in converters, heat exchangers, and absorbers.

ATMOSPHERIC EMISSIONS (Ref. 5, 6, and 7)

The emissions from sulfuric acid plants are sulfur dioxide, acid with acid mist causing opacity. Organic compounds, nitrogen oxides, and nitrosyl sulfuric acid also appear at the exhaust stack exit along with water vapor not removed by the drying tower and acid mist plumes.

Sulfur Dioxide Emissions

The sulfur dioxide emitted from the plant stack as effluent is the product from the sulfur furnace that was not converted to sulfur trioxide in the catalytic converter. This unconverted sulfur dioxide is not absorbed in the absorber tower and is contained in the vent gas. Primary reasons for SO_2 not being converted to sulfur trioxide are caused by inactive or poisoned catalyst, insufficient process air for the catalytic conversion to sulfur trioxide, or improper catalyst bed temperatures.

Acid Mist Emissions (Ref. 8 and 9)

The acid mist emitted from the plant results from (1) liquid sulfuric acid carryover from absorbers; (2) sulfur trioxide in the converter reacting with the water vapor in the process gas system preceding the converter thus producing sulfuric acid mist; and (3) unabsorbed sulfur trioxide reacting with atmospheric moisture. The water vapor in the process gas can come from insufficient drying of combustion air, air leaks, steam or boiler feed water leaks or combustion of organics in the sulfur furnace feed.

Nitrogen Oxides Emissions

Yellow vapors indicate small quantities of nitrogen oxides may be present in sulfuric acid plant vent gases. Nitrogen oxides can come from high temperatures and usually occur when sulfur impinges on the furnace walls or floor, or from the combustion of organic nitrogen compounds in the furnace. Small quantities may be produced but will increase opacity. There is no standard restricting the nitrogen oxides from the sulfuric acid plants except indirectly through plume opacity.

Plume Opacity (Ref. 8 and 9)

The opacity of the vent gas from a sulfuric acid plant must be less than 10 percent unless the plume consists of uncombined water only. The presence of acid mist, water vapor and nitrogen oxides will contribute to plume opacity. The effect of acid mist on opacity is more dependent on the size of the mist particles than the quantity of mist. The mist size usually ranges from 0.3 to 3.0 microns. Factors such as concentration and temperature of absorber acid and nitrogen content of feed stock affect the quantity and size of mist. The smaller particles scatter light more, producing a denser plume. The effect of water vapor on plume opacity is also more dependent on particle size than quantity. Nitrogen oxides will add yellow vapors to the plume. The effect will vary from a very slight yellowish tinge to a definite yellow cast.

Careful plant operation can minimize the effect of process conditions that cause acid mist, excess water vapor, and nitrogen oxides, and keep the plume opacity below the standard limits.

EMISSION CONTROL METHODS

Sulfur Dioxide Control Methods (Ref. 10, 11, 12, 13, 14, and 15)

The typical single absorption contact sulfuric acid plant is not capable of meeting the current sulfur dioxide emission standards when using an economically feasible converter design. The minimum sulfur dioxide concentration in the vent gas is limited by equilibrium conditions within the catalytic converter and the amount of catalyst that can be installed economically in the plant. Because of these limitations the single absorption sulfuric plant must be equipped with sulfur dioxide removal systems to reduce the vent gas sulfur dioxide concentration to an acceptable level.

Many processes have been proposed to perform this operation, but only three have been included in this manual: sodium sulfite scrubber, ammonia scrubber, and molecular sieve absorption.

Sodium Scrubber System (Ref. 16)

The sodium scrubber process is a wet regenerative system based on a sodium sulfite/bisulfite cycle.

The system includes absorber and chemical regeneration processes. The reactions that take place in the process can be simplified to the following:

Absorption: $SO_2 + Na_2SO_3 + H_2O$ -- $2NaHSO_3$

Regeneration: $2NaHSO_3$ -- $Na_2SO_3 + SO_2 + H_2O$

The process flow diagram is shown in Figure 3.

The sulfur dioxide rich gas is contacted counter-currently in the absorber by the sodium sulfite solution and passes out the top stripped of sulfur dioxide. (An absorber with inlet concentration of 1560 parts per million sulfur dioxide and a 95 percent scrubber efficiency can achieve an emission level of 86 parts per million sulfur dioxide).

The condensate is recycled to the dissolving tank and the product, sulfur dioxide gas, is recycled to the sulfuric acid plant or claus elemental sulfur plant.

The rich slurry of sodium sulfate purged from the scrubbing system is either (1) directly discharged to the river stream for small plants and small quantities, or (2) the slurry is dried for direct sale to paper pulp mills.

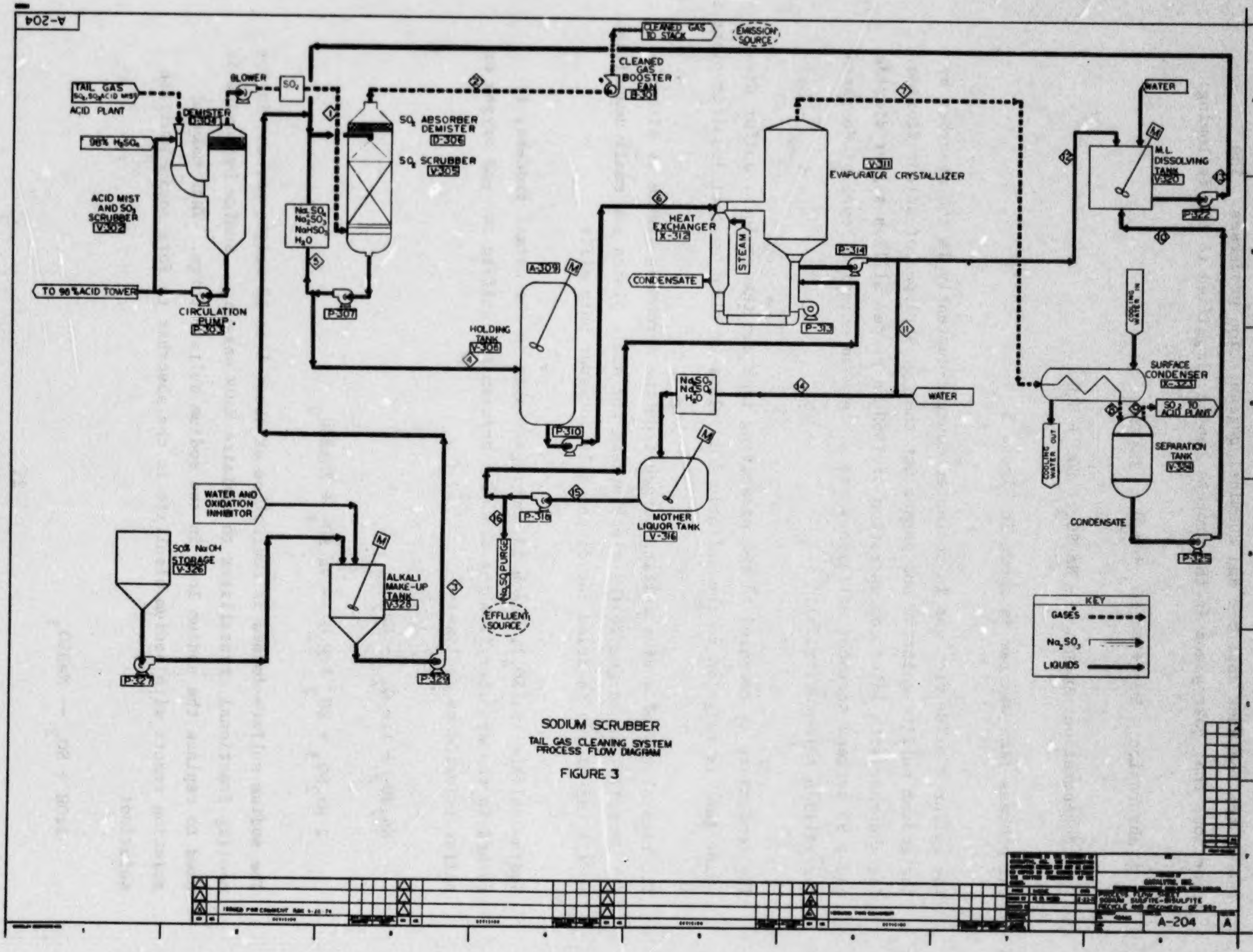
Sodium sulfate (Na_2SO_4), which is non-regenerable in the normal process, is formed in the absorber from the reaction between the sulfite ion and oxygen or sulfur trioxide as follows:

$Na_2SO_3 + 1/2\ O_2$ -- Na_2SO_4

$2\ Na_2SO_3 + SO_3 + H_2O$ -- $Na_2SO_4 + 2NaHSO_3$

The sodium sulfate formed is controlled at about 5 to 10 weight percent in the cooling fractional crystallizer to minimize NaOH makeup. Sodium hydroxide is used to replace the sodium lost in the sodium sulfate purge. This make-up solution reacts with sodium bisulfite in the absorber to form sodium sulfite solution:

$NaOH + SO_2$ -- $NaHSO_3$


A-204
TAIL GAS
SO_3, SO_2, ACID MIST
ACID PLANT
DEMISTER
D-304
BLOWER
SO_2
98% H_2SO_4
ACID MIST AND SO_3 SCRUBBER
V-302
TO 98% ACID TOWER
CIRCULATION PUMP
P-303
SO_2 ABSORBER DEMISTER
D-306
SO_2 SCRUBBER
V-305
Na_2SO_4
Na_2SO_3
$NaHSO_3$
H_2O
P-307
CLEANED GAS TO STACK
EMISSION SOURCE
CLEANED GAS BOOSTER FAN
B-301
HOLDING TANK
V-308
A-309
M
P-310
HEAT EXCHANGER
X-312
STEAM
CONDENSATE
V-311
EVAPORATOR CRYSTALLIZER
P-313
P-314
WATER
Na_2SO_3
Na_2SO_4
H_2O
MOTHER LIQUOR TANK
V-316
P-316
Na_2SO_4 PURGE
EFFLUENT SOURCE
WATER AND OXIDATION INHIBITOR
50% NaOH STORAGE
V-326
P-327
ALKALI MAKE-UP TANK
V-328
P-329
M.L. DISSOLVING TANK
V-320
P-322
COOLING WATER IN
COOLING WATER OUT
SURFACE CONDENSER
X-323
SO_2 TO ACID PLANT
SEPARATION TANK
V-324
CONDENSATE
P-325
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
KEY
GASES
Na_2SO_3
LIQUIDS
SODIUM SULFITE-BISULFITE
A-204
A

SODIUM SCRUBBER

TAIL GAS CLEANING SYSTEM
PROCESS FLOW DIAGRAM

FIGURE 3

Ammonia Scrubber System (Ref. 17, 18, and 19)

Commercial ammonia scrubber processes based on the same chemical reactions are available from several design companies.

The ammonia scrubber uses a solution of ammonium sulfite to form ammonium bisulfite. The ammonium bisulfite is regenerated by reaction with ammonia to form ammonium sulfite. The equations for the two reactions are:

$$SO_2 + (NH_4)_2SO_3 + H_2O \text{ -- } 2NH_4HSO_3$$

$$NH_3 + NH_4SO_3 \text{ -- } (NH_4)_2SO_3$$

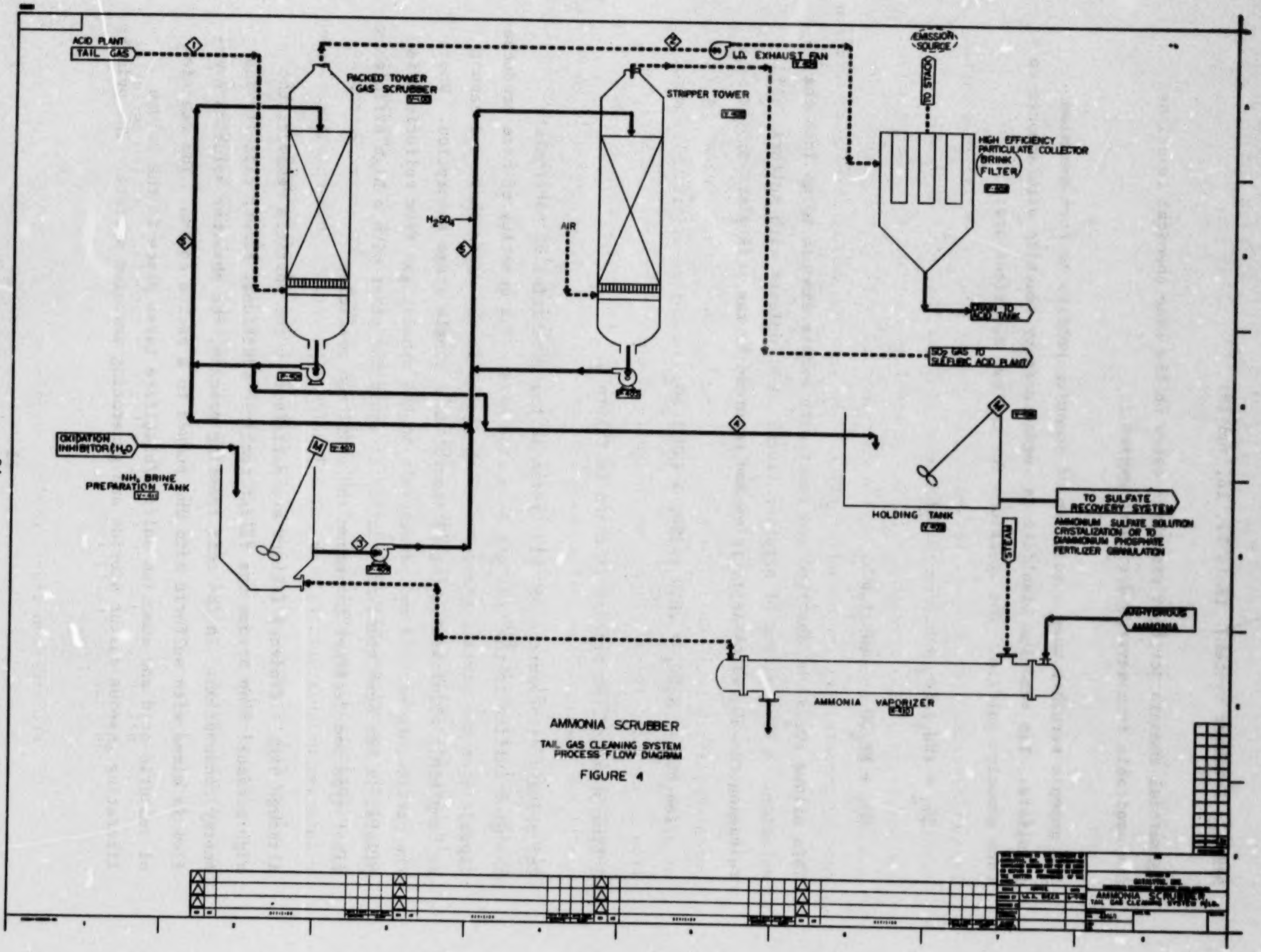
This allows SO_2 to be absorbed and react with excess ammonia to go into the solution. A slip stream of scrubber liquid is acidulated with sulfuric acid releasing the SO_2 which is recycled and returned to the acid plant system.

$$2NH_4HSO_3 + H_2SO_4 = 2H_2O + 2SO_2 + (NH_4)_2SO_4$$

A flow sheet of the process is shown in Figure 4.

The primary disadvantage of this system is the generation of particulate ammonium sulfite in the vent gas as a blue haze. The quantity of haze produced depends upon the partial pressures of the gases in the vapor phase and cannot be completely eliminated using pH control in a single stage absorption. Where the particulate haze is not permissible in the exhaust gas from sulfuric acid plants, it has been standard practice to equip the plant with a high efficiency fiber type pad demister to remove the submicron particles.

Although high efficiency filters are satisfactory for particle removal, the high pressure drop across the filter requires additional blower capacity and energy consumption. In the acid treating process, the absorber solution overflow is mixed with sulfuric acid and pumped to a packed column. The reaction of sulfuric acid and ammonium sulfite/bisulfite takes place in the column liberating gaseous sulfur dioxide and generating ammonium sulfate. The primary


ACID PLANT
TAIL GAS
1
PACKED TOWER
GAS SCRUBBER
2
I.D. EXHAUST FAN
STRIPPER TOWER
EMISSION SOURCE
TO STACK
HIGH EFFICIENCY
PARTICULATE COLLECTOR
(BRINK FILTER)
DRAIN TO ACID TANK
SO2 GAS TO SULFURIC ACID PLANT
H2SO4
AIR
5
5
4
3
M
M
OXIDATION INHIBITOR(H2O)
NH3 BRINE
PREPARATION TANK
HOLDING TANK
TO SULFATE RECOVERY SYSTEM
AMMONIUM SULFATE SOLUTION
CRYSTALIZATION OR TO
DIAMMONIUM PHOSPHATE
FERTILIZER GRANULATION
STEAM
ANHYDROUS AMMONIA
AMMONIA VAPORIZER
AMMONIA SCRUBBER
TAIL GAS CLEANING SYSTEM P.F.D.

AMMONIA SCRUBBER

TAIL GAS CLEANING SYSTEM
PROCESS FLOW DIAGRAM

FIGURE 4

reactions of the process are shown in these equations:

$$(NH_4)_2SO_3 + H_2SO_4 \text{ -- } (NH_4)_2SO_4 + H_2O + SO_2$$

$$2NH_4HSO_3 + H_2SO_4 \text{ -- } (NH_4)_2SO_4 + 2H_2O + 2SO_2$$

The sulfur dioxide is recycled to the sulfuric acid plant while the ammonium sulfate solution is collected for further processing.

Various processes are used for reclaiming the sulfur from the absorber solution overflow. These include treating with sulfuric acid, to release SO_2 about 20-25 percent by volume and ammonium sulfate. Thermal decomposition of the resulting ammonium sulfate to ammonium bisulfite and ammonia gas is in pilot plant development by Tennessee Valley Authority (TVA). The ammonium sulfite/bisulfite solution also may be added.

The ammonium sulfate solution is concentrated and crystallized to produce solid ammonium sulfate or is used in mixed fertilizers. When the acid plant is a part of a fertilizer complex, the ammonium sulfate or ammonium sulfite/sulfate solution is included in the diammonium phosphate production process. Mixing the ammonium sulfate solution in fertilizer provides a low cost outlet with a secondary use of the ammonia. The sulfur content of the solution is also valuable as a plant nutrient. Thus, the ultimate disposal of waste products is recycled back to the soil as fertilizer.

Molecular Sieve Adsorption Process (Ref. 19 and 20)

One of the newest sulfur dioxide recovery processes to be applied commercially to sulfuric acid plant vent gas is the molecular sieves. Molecular sieves are substances which selectively absorb molecules with certain characteristics, such as shape and polarity. The adsorption cycle is followed by desorption, with an air stream or some other gas, during which the molecular sieve is regenerated. A number of molecular sieves are commercially available for the removal of SO_2 from the tail gas. Features of such a system are:

1. High sulfur dioxide removal efficiency especially at low sulfur dioxide concentrations.

2. Freedom from liquid handling problems.

3. Absence of waste products.

4. Simple operation.

The adsorption efficiency of the molecular sieves is not dependent upon flow rate or concentration of sulfur dioxide. Normal upsets in acid plant operations do not affect the concentration of sulfur dioxide in the gas leaving the molecular sieve system. Carbon dioxide and nitrogen oxides in vent gas from burning acid sludge or dirty sulfur do not affect the adsorption efficiency of the molecular sieves system.

A process flow diagram for the molecular sieve sulfur dioxide recovery system is shown in Figure 5.

The exit gas from the molecular sieve tower contains 15 to 20 parts per million sulfur dioxide (and normally 0-10 ppm after breakthrough).

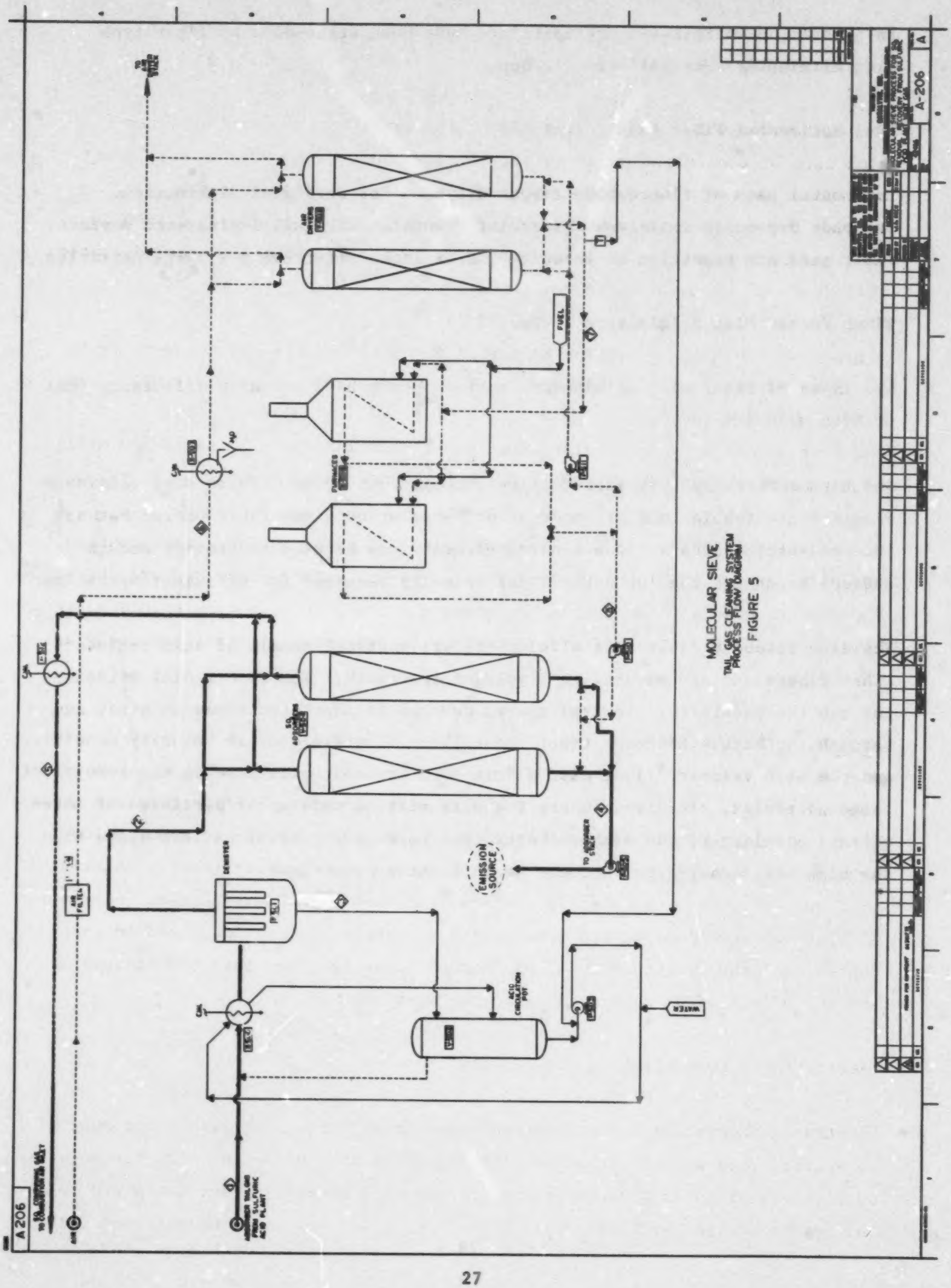
The addition of the stripping air from molecular sieve regeneration, containing 20 to 30 percent SO_2 is charged to the gas leaving the furnace and will vary the sulfur dioxide concentration entering the converter. During normal operation this variation of sulfur dioxide entering the converter does not adversely affect the process.

Acid Mist Control Methods (Ref. 8 and 9)

Removal of acid mist from the vent gas requires techniques different from those used for sulfur dioxide emissions and scrubber systems. The molecular sieve systems are equipped to remove acid mist before the adsorber tower. Additional mist removal equipment is not necessary with these systems. Earliest mist eliminators were beds packed with saddle or pebble packing installed in the outlet of absorption towers. These remove spray (greater than ten microns) but are not effective on mist (less than ten microns).

Electrostatic Precipitators (Ref. 21)

Electrostatic precipitators have been used in sulfuric acid plants for about 65 years. They are effective in removing spray and in process mist for moderate to light loadings in preburning and gas cleaning stages. Power costs are nominal. The drawbacks are the large size, high first cost, and heavy maintenance cost.


A 206
TO CONVERTER INLET
ABSORBER TAIL GAS FROM SULFURIC ACID PLANT
AIR FILTER
DEMISTER
ACID CIRCULATION POT
WATER
EMISSION SOURCE
TO ABSORBER STACK
SO2 ADSORBERS
FURNACES
FUEL
A-206
A

MOLECULAR SIEVE
TAIL GAS CLEANING SYSTEM
PROCESS FLOW DIAGRAM
FIGURE 5

In general, electrostatic precipitators have been superseded by fiber type mist eliminators for tail gas cleanup.

Dual Horizontal Fiber Pads (Ref. 22)

Horizontal pads of fluorcarbon fibers are used for acid mist elimination. The pads depend on impingement for mist removal. Like all impingement devices, fiber pads are sensitive to velocity and are more effective for large particles.

Fiber Packed Mist Eliminators (Ref. 22)

Two types of fiber mist eliminators most commonly used are high efficiency (HE) or high velocity (HV).

The high efficiency type is effective for mist and spray. These mist eliminator elements are tubular and are made of acid-resistant glass fiber packed between two concentric screens. One hundred elements may be used to provide enough surface to ensure the low superficial velocity required for efficient operation.

The high velocity fiber mist eliminators are vertical panels of acid-resistant glass fibers and are mounted in a polygon framework. The superficial velocity through the panels (of the impingement device) is about ten times as great as through the high efficiency type; the collection efficiency is velocity sensitive; and the high velocity fiber mist eliminators are most effective in the removal of large particles. In plants where the acid mist is made up of particles of three microns and larger, the high velocity type works well, requires less space than the high efficiency type, and can be built at a lower cost.

SECTION 4

INSTRUMENTATION RECORDS AND REPORTS

PROCESS INSTRUMENTATION

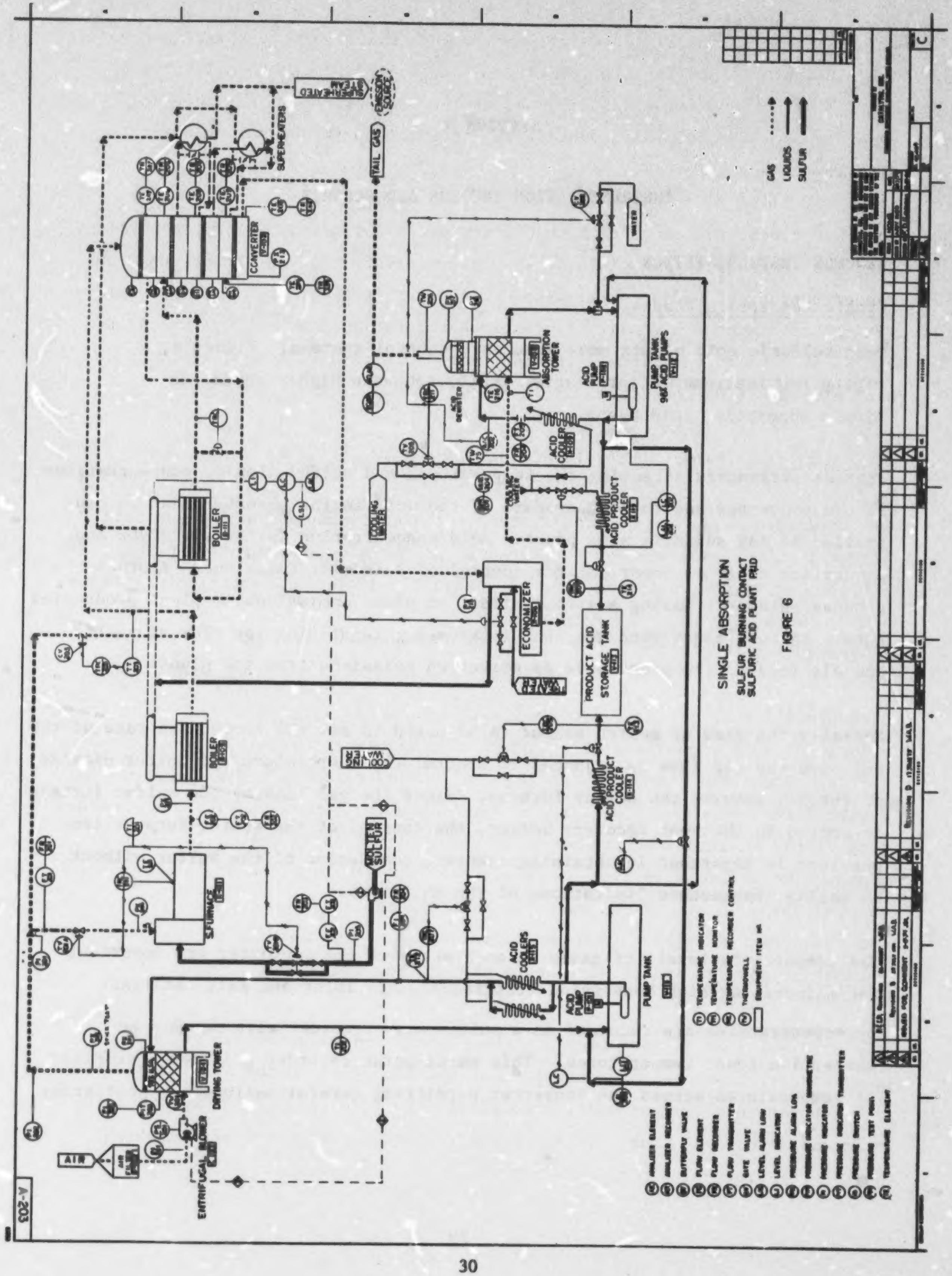
Single Absorption Plants

Most sulfuric acid plants have automatic control systems. Figure 6, a piping and instrumentation diagram (P&ID), shows a highly automated single absorption acid plant.

Process parameters affecting the temperatures and sulfur dioxide concentrations in the converter and the temperature of the acid in the absorber must be controlled in any sulfuric acid plant. Acid concentration in the air dryer and absorption tower is important for control of acid mist emissions. Another process parameter having a strong effect on plant emmissions is plant production rate. In compliance with EPA, the instruments regulating the flow of sulfur and air feed to the plant have an effect on emissions from the plant.

Normally the flow of molten sulfur is adjusted to set the production rate of the unit and the air flow is adjusted to control the temperature and sulfur dioxide of the gas leaving the sulfur furnace. Since the gas leaving the sulfur furnace is cooled in the heat recovery boiler, the control of the sulfur furnace temperature is important in obtaining complete combustion of the sulfur without exceeding temperature limitations of the equipment.

The temperature levels of gases in each stage of the converter are important for maintaining high conversion efficiency. All inlet and exit catalyst bed temperatures are recorded on a multi-point recorder with furnace and absorption tower temperatures. This multi-point recorder provides a profile of temperatures across the converter permitting careful malfunction monitoring


A-203
AIR
AIR FILTER
CENTRIFUGAL BLOWER
DRYING TOWER
S.FURNACE
BOILER
CONVERTER
SUPERHEATERS
SUPERHEATED STEAM
TAIL GAS
MOLTEN SULFUR
COOLING WATER
ECONOMIZER
TREATED WATER
PRODUCT ACID STORAGE TANK
ACID PRODUCT COOLER
ACID COOLERS
ACID COOLER
ACID PUMP
PUMP TANK
98% ACID PUMPS
ABSORPTION TOWER
WATER
GAS
LIQUIDS
SULFUR
TEMPERATURE INDICATOR
TEMPERATURE MONITOR
TEMPERATURE RECORDER CONTROL
THERMOWELL
EQUIPMENT ITEM NO.
ANALYZER ELEMENT
ANALYZER RECORDER
BUTTERFLY VALVE
FLOW ELEMENT
FLOW RECORDER
FLOW TRANSMITTER
GATE VALVE
LEVEL ALARM LOW
LEVEL INDICATOR
PRESSURE ALARM LOW
PRESSURE INDICATOR CONTROLLER
PRESSURE INDICATOR
PRESSURE INDICATING TRANSMITTER
PRESSURE SWITCH
PRESSURE TEST POINT
TEMPERATURE ELEMENT
C

SINGLE ABSORPTION

SULFUR BURNING CONTACT
SULFURIC ACID PLANT P&ID

FIGURE 6

and assisting in the diagnosis of problems affecting converter efficiency. Information obtained from the multi-point recorder is used to adjust manual control valves and setpoints of automatic control systems. Reliable and accurate operation of this recorder is important to the operation of the plant with low emission levels.

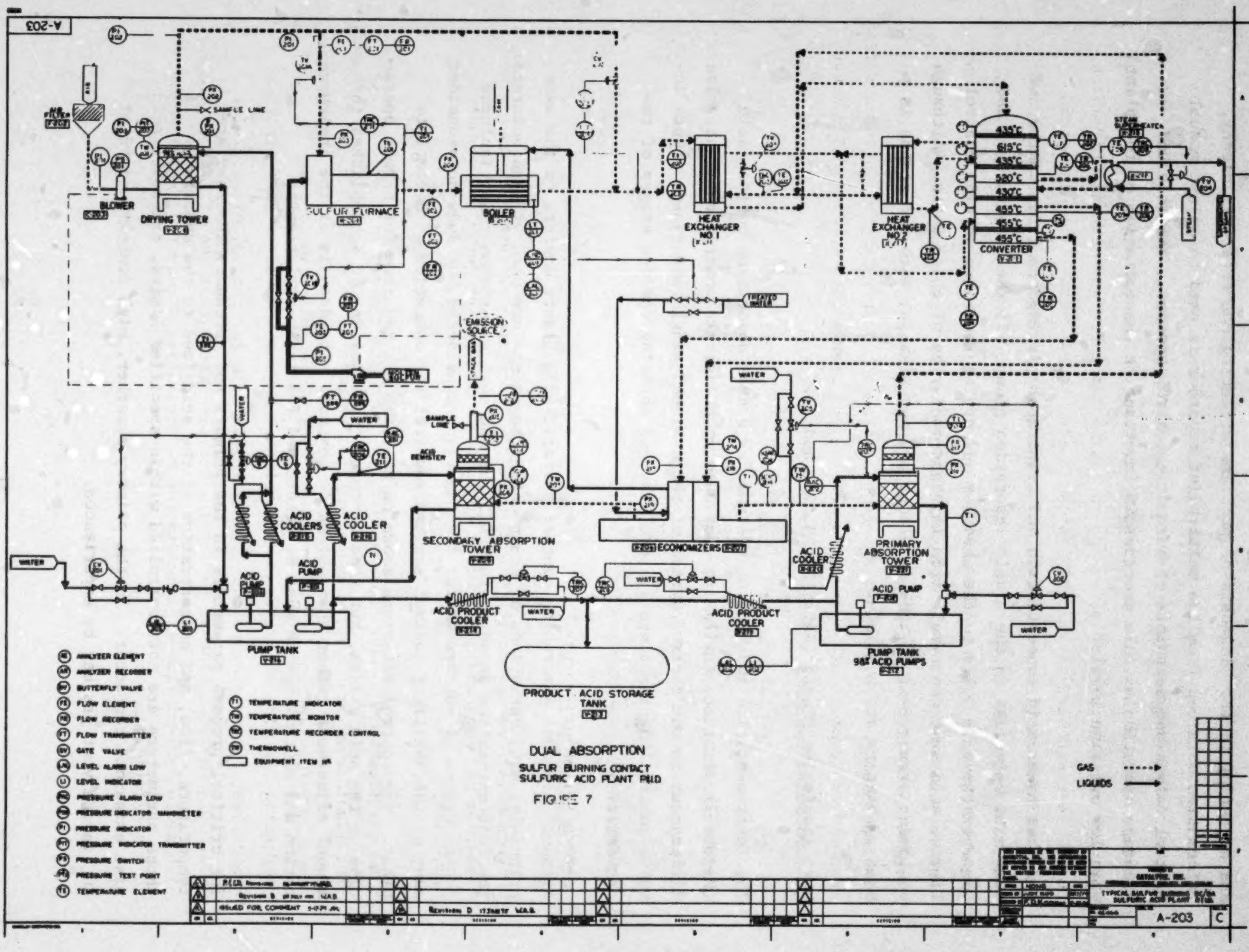
Absorber tower acid concentration and temperature is important for control of acid mist emissions in the single absorption plant. If the temperatures and concentrations of acids to the absorber and drying tower are outside control limits, acid mist can result from improper operation of these units. Although equipment arrangement designs in plants are not sizable, some variations in heat exchangers are possible.

Dual Absorption Plants (Ref. 15, 23, 24, and 25)

The instrumentation and control systems for a dual absorption contact acid (Figure 7) plant are similar to that used on the single absorption plant. The differences in the control system of the dual and single absorption plants involve controlling the temperature of the gas entering various stages of the converter.

Although all dual absorption contact sulfuric acid plants operate on the same principle, many variations of equipment arrangements are used by manufacturers. The instrumentation shown on the P&ID for the dual absorption plant includes a high degree of automation for the functions considered but does not consider many of the auxiliary control systems required for operation of a complete plant. The control functions shown on the P&ID are required for normal operation of the acid plants, but some of these functions may be accomplished through manual adjustment rather than automatic control. The details of the instrumentation and control system must be determined for individual plants.

The critical process parameters in the primary and secondary absorber are temperature, flow, and concentration of the acid feed to the absorbers. If these parameters are not controlled within specified limits, excessive acid mist emissions can occur. In the primary absorber, high concentrations of SO_2 in the vent gas may be experienced.


A-203
AIR
AIR FILTER
BLOWER
DRYING TOWER
SAMPLE LINE
SULFUR FURNACE
BOILER
HEAT EXCHANGER NO 1
HEAT EXCHANGER NO 2
CONVERTER
435°C
615°C
435°C
520°C
430°C
455°C
455°C
455°C
STEAM SUPERHEATER
STEAM
TREATED WATER
EMISSION SOURCE
STACK GAS
MOLTEN SULFUR
WATER
SAMPLE LINE
ACID DEMISTER
SECONDARY ABSORPTION TOWER
ECONOMIZERS
PRIMARY ABSORPTION TOWER
ACID COOLERS
ACID COOLER
ACID PUMP
H_2O
PUMP TANK
ACID PRODUCT COOLER
PRODUCT ACID STORAGE TANK
PUMP TANK 98% ACID PUMPS
ANALYZER ELEMENT
ANALYZER RECORDER
BUTTERFLY VALVE
FLOW ELEMENT
FLOW RECORDER
FLOW TRANSMITTER
GATE VALVE
LEVEL ALARM LOW
LEVEL INDICATOR
PRESSURE ALARM LOW
PRESSURE INDICATOR MANOMETER
PRESSURE INDICATOR
PRESSURE INDICATOR TRANSMITTER
PRESSURE SWITCH
PRESSURE TEST POINT
TEMPERATURE ELEMENT
TEMPERATURE INDICATOR
TEMPERATURE MONITOR
TEMPERATURE RECORDER CONTROL
THERMOWELL
EQUIPMENT ITEM NO.
GAS
LIQUIDS
P&ID Revised
Revision B
ISSUED FOR COMMENT
Revision D
TYPICAL SULFUR BURNING DC/DA SULFURIC ACID PLANT P&ID
A-203
C

DUAL ABSORPTION
SULFUR BURNING CONTACT
SULFURIC ACID PLANT P&ID

FIGURE 7

The temperature of acid feed to the primary and secondary absorber and the drying tower is normally controlled by adjusting the water flow to the acid coolers feeding these units. These controls may be manual or automatic. The primary and secondary absorbers operate with concentrated sulfuric acid which must be controlled within the proper concentration range to maintain acid mist emissions at the required level. The acid circulating in the final absorption tower is passed through the drying tower to remove moisture from the air feed to the sulfur furnace and converter. The acid concentration in the primary and the secondary absorber systems is maintained by analyzers in each system controlling dilution water feed to the system. Control of acid concentrations is important. If an automatic control system is not installed or is inoperative, manual acid concentration analysis must be run frequently to permit adjustment of the water addition to the absorber tower systems.

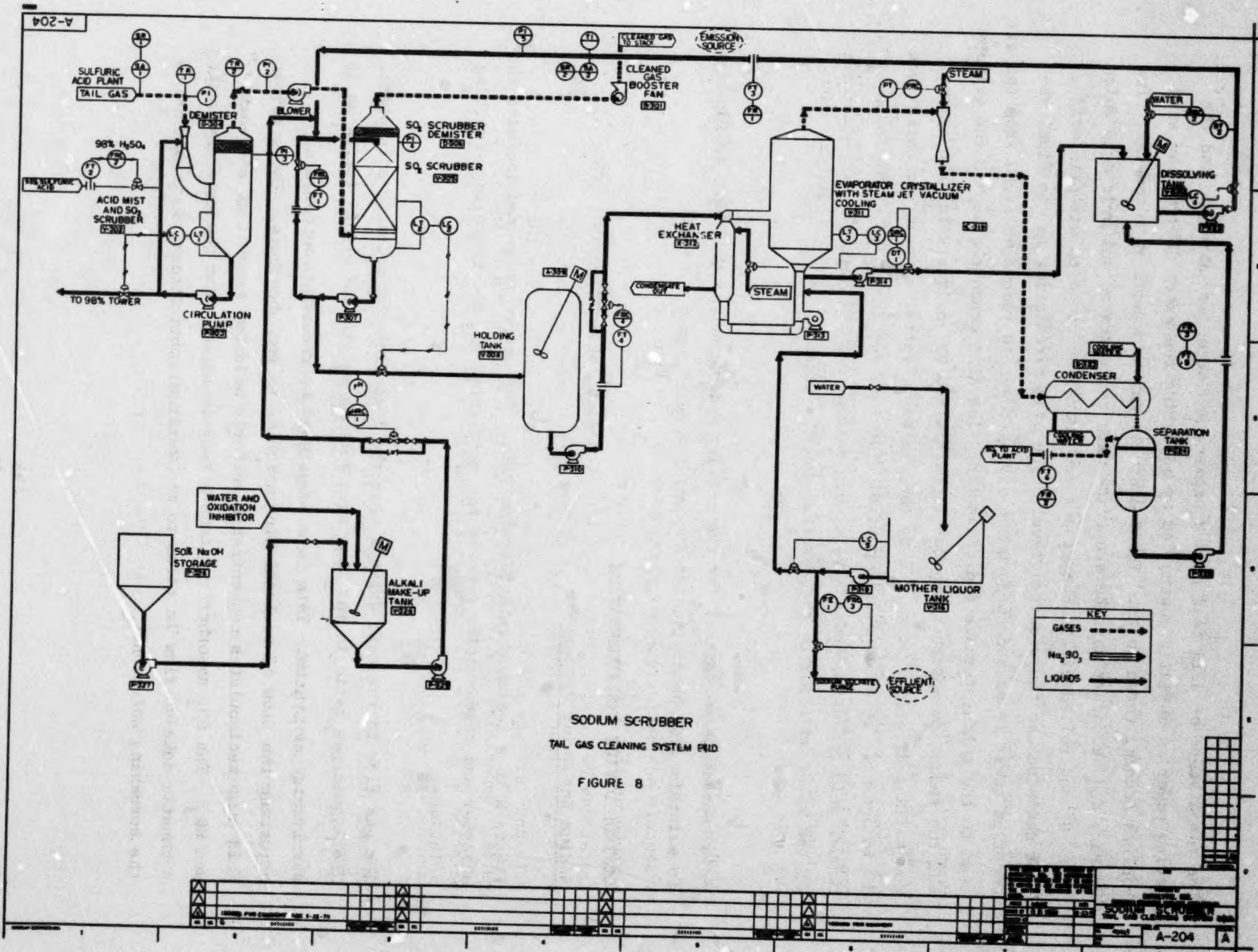
Acid concentration control for the primary and secondary absorbers is important to maintain good absorption of SO_3 and a "clear" stack condition.

CONTROL DEVICE INSTRUMENTATION

Sodium Scrubbing Process

Figure 8 is a sodium scrubber system P&ID. The system presented includes the absorber and regeneration process for recovering SO_2 and recycling scrubbing solution.

The gas flow to the unit depends upon the load from the sulfuric acid plant. The liquid/gas ratio in the absorbers must be maintained within limits as in any liquid/gas system. This is accomplished by recorder controllers adjusting the flow of recirculating solution to the absorbers. The scrubber acid pump recirculates concentrated sulfuric acid for removal of acid mist and SO_3. The SO_2 absorber receives a recycle stream from the recovery system. A caustic make-up flow is added to the recirculating stream to control pH of the scrubbing solution.


A-204
SULFURIC ACID PLANT TAIL GAS
DEMISTER
98% H_2SO_4
98% SULFURIC ACID
ACID MIST AND SO_2 SCRUBBER
TO 98% TOWER
CIRCULATION PUMP
BLOWER
SO_2 SCRUBBER DEMISTER
SO_2 SCRUBBER
CLEANED GAS TO STACK
EMISSION SOURCE
CLEANED GAS BOOSTER FAN
HOLDING TANK
M
CONDENSATE OUT
HEAT EXCHANGER
STEAM
EVAPORATOR CRYSTALLIZER WITH STEAM JET VACUUM COOLING
WATER
DISSOLVING TANK
COOLING WATER
CONDENSER
SEPARATION TANK
SO_2 TO ACID PLANT
WATER AND OXIDATION INHIBITOR
50% NaOH STORAGE
ALKALI MAKE-UP TANK
MOTHER LIQUOR TANK
SODIUM SULFATE PURGE
EFFLUENT SOURCE
KEY
GASES
Na_2SO_3
LIQUIDS
A-204
A

SODIUM SCRUBBER

TAIL GAS CLEANING SYSTEM P&ID

FIGURE 8

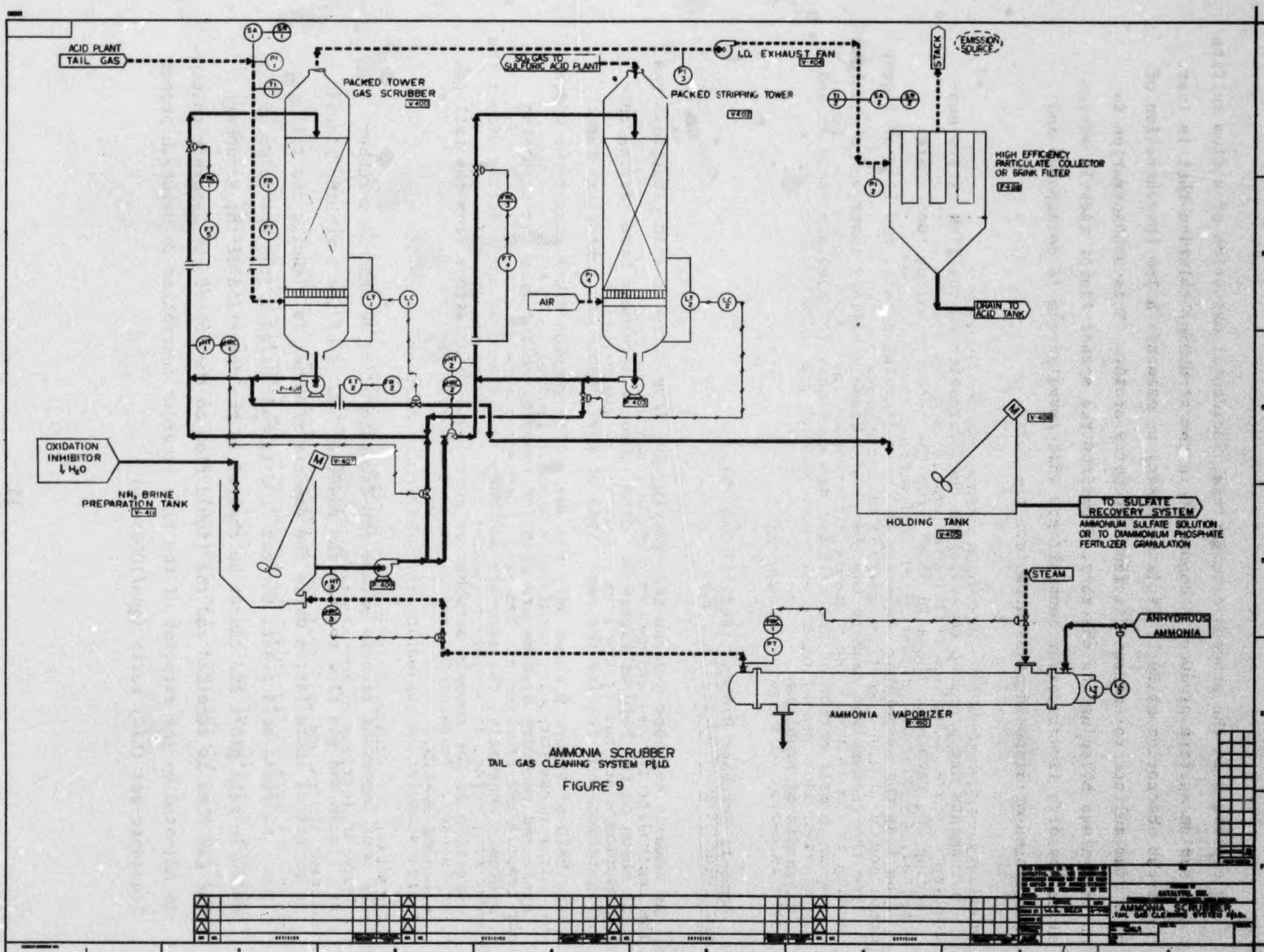
As explained in the process descriptions, incidental oxidation of sodium sulfite to sodium sulfate produces a component in the scrubbing solution that is inert in the absorption of SO_2. It is necessary to maintain a low concentration of sodium sulfate to ensure efficient scrubbing of SO_2. This concentration is maintained by adjusting the purge flow from the mother liquor recycle stream by use of a flow recorder controller. This purge stream is decomposed and recycled or disposed of as a waste.

Instruments are provided to assist in the evaluation of the flow meters measuring SO_2 return to the acid plant from the recovery units, condensate flow from the evaporator condenser to the redissolving tank, and flow of liquor from the redissolver tank to the absorber. These auxiliary instruments should not cause malfunction of the unit but are necessary for adequate analysis and diagnosis of problems.

Ammonia Scrubber Process (Ref. 17 and 19)

An ammonia scrubber process for removing SO_2 from sulfuric acid plant tail gas is shown on the P&ID of Figure 9. Other ammonia scrubbers have varying configurations but require the same types of instruments and control systems. The P&ID of Figure 9 shows only the absorption section since many types of recycle and recovery systems are used for removing sulfur from the scrubbing system. Generally, the recovery and recycle system does not directly affect the operation of the ammonia scrubber or contribute to emissions from the tail gas cleaning system.

The most important process parameters encountered in an ammonia scrubber are liquid and gas flow through the adsorber and pH of the scrubbing liquid. In practical installation where the ammonia scrubber is cleaning the tail gas from a sulfuric acid plant, the gas flow is controlled by the operation of the sulfuric acid plant and cannot be changed in the operation of the scrubber. The gas flow is recorded and the liquid flow to the top of the absorber column is adjusted by the setpoint of the flow recorder controller to maintain proper liquid-to-gas (L/G) ratio (gpm/1000scfm).


ACID PLANT
TAIL GAS
SA 1
SR 1
PI 1
TI 1
FR 1
FT 1
FRC 1
FT 5
PACKED TOWER
GAS SCRUBBER
V-400
SO₂ GAS TO
SULFURIC ACID PLANT
PI 3
I.D. EXHAUST FAN
V-404
STACK
EMISSION
SOURCE
PACKED STRIPPING TOWER
V-401
TI 2
SA 2
SR 2
PI 2
HIGH EFFICIENCY
PARTICULATE COLLECTOR
OR BRINK FILTER
F-408
DRAIN TO
ACID TANK
FRC 3
FT 4
PI 4
AIR
LT 1
LC 1
LT 2
LC 2
pHT 1
pHRC 1
pHT 2
pHRC 2
P-401
FT 2
FR 2
P-403
OXIDATION
INHIBITOR
& H₂O
NH₃ BRINE
PREPARATION TANK
V-411
M
V-407
pHT 3
pHRC 3
P-409
M
V-406
HOLDING TANK
V-405
TO SULFATE
RECOVERY SYSTEM
AMMONIUM SULFATE SOLUTION
OR TO DIAMMONIUM PHOSPHATE
FERTILIZER GRANULATION
STEAM
PRC 1
PT 1
ANHYDROUS
AMMONIA
LT 3
LC 3
AMMONIA VAPORIZER
E-410
CATALYTIC, INC.
AMMONIA SCRUBBER
TAIL GAS CLEANING SYSTEM P&ID

AMMONIA SCRUBBER
TAIL GAS CLEANING SYSTEM P&ID

FIGURE 9

Efficient adsorption of SO_2 in the ammonia scrubber depends upon maintaining proper pH in the scrubbing liquid, the pH value normally ranges from 5.8 to 6.0. Careful control of ammonia flow and concentration is required to obtain efficient scrubbing in the absorber. This control system is very important since loss of availability of ammonia gas will result in lower pH scrubbing solutions and excess SO_2 emissions from the unit.

Auxiliary equipment in the ammonia scrubbing system includes: (1) sulfur analyzers on the inlet and outlet gaslines to show the amount of SO_2 removal obtained, (2) pressure differential indicators across the columns to show the condition of column operation, and (3) pressure gages to indicate the gas loading in the column. The pressure differential indicators across the column are of value when operating the absorbers at high gas velocities and where there is danger of flooding the column.

Molecular Sieve Process (Ref. 20)

The controller for this system is a cycle timer to sequence valves to switch SO_2 absorbers and air dryers from absorption to regeneration.

The main process parameter requiring automatic control is the regenerating air temperature from the air heaters. Air temperature is controlled by a recorder controller, if a steam preheater is used, or by the fuel flow to a fuel fired furnace. Temperature indicators in the sulfur dioxide adsorbers and the air dryers assist in evaluating the performance of these desiccant beds and in determining the degree of saturation during the adsorption cycle. Differential pressure indications across the beds provide evaluation of the condition of the desiccant charge and will help guard against excessive flow rates.
Sulfur analyzers on the inlet and outlet streams from the SO_2 absorbers indicate the overall sulfur removal efficiency. The P&ID of Figure 10 shows the simplified form of the basic instrumentation for this process.

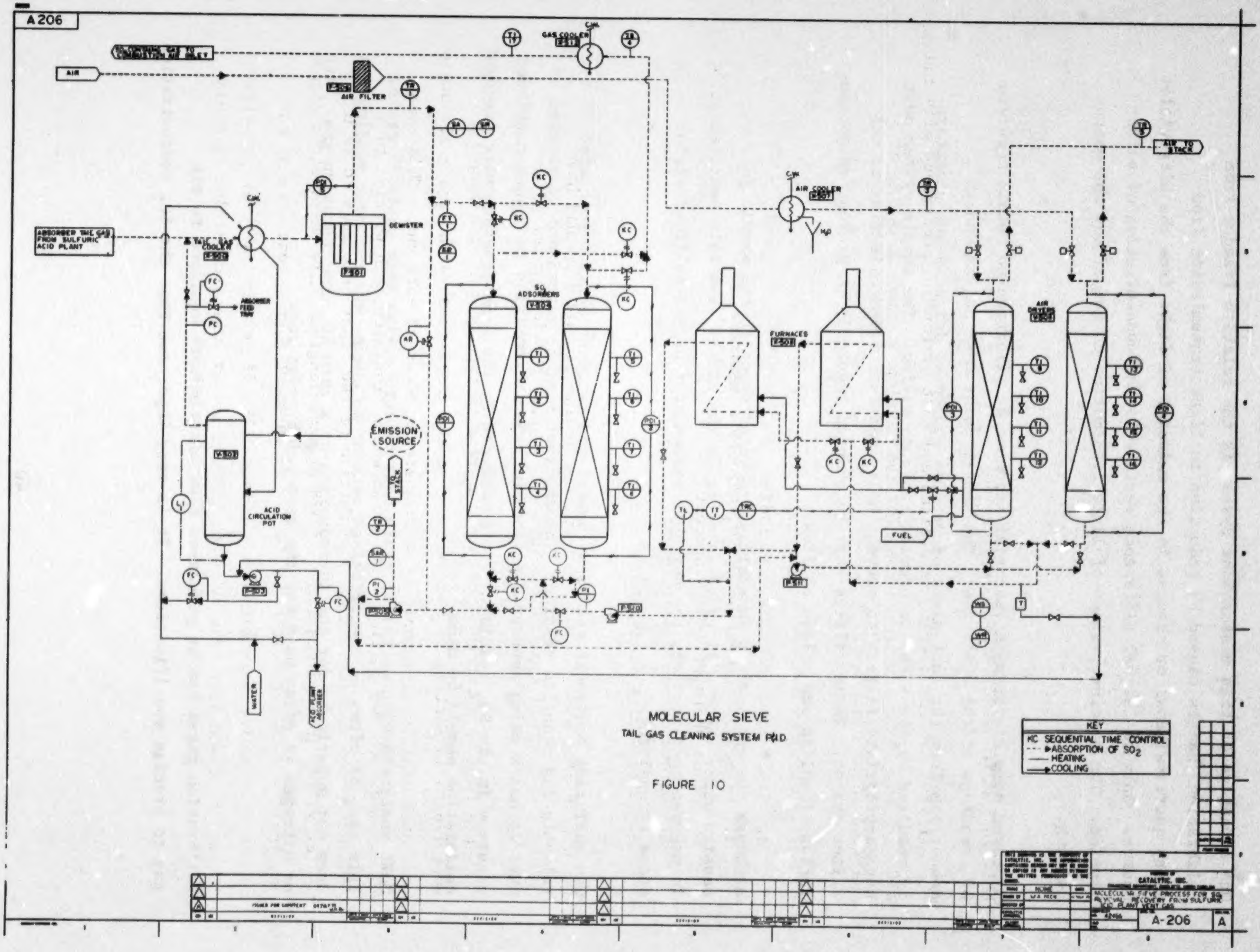
EMISSIONS MONITORING INSTRUMENTATION (Ref. 26)

The emission monitor must be maintained and must perform in accordance with the NSPS. Measurement principles used for the development and marketing of gas analysis instruments are:

1. Infra-red absorption
2. Colormetric titration of iodine
3. Selective permeation of SO_2 through a membrane
4. Flame photometric measurement
5. Chromatographic measurement
6. Ultraviolet absorption

The ultraviolet absorption system and the iodine titration method have received widespread application in modern sulfuric acid plants.

The principle of ultraviolet absorption by each type of gas at a specific wave length is applied in the analyzer as the gas is passed through a 316 stainless steel sample tube equipped with quartz windows at each end. This beam is divided into two portions by a prism which transmits each portion to a separate photo detector tube. One portion of the light beam goes to an ultraviolet filter that passes light of 578 nm wave length. This photometric signal is the reference for comparison to the measurement signal generated by the second ultraviolet beam going to a filter. The difference in these two signals is amplified and sent to a recorder through proper signal conditioning equipment.


A 206
AIR
AIR FILTER
GAS COOLER
C.W.
ABSORBER TAIL GAS FROM SULFURIC ACID PLANT
TAIL GAS COOLER
DEMISTER
F-501
ABSORBER FEED TRIM
FC
PC
SO2 ADSORBERS
V-504
KC
TI
PDI
FT
AR
SA
SAR
TR
PI
EMISSION SOURCE
STACK
V-503
ACID CIRCULATION POT
LI
WATER
ACID PLANT ABSORBER
FURNACES
F-502
FUEL
TRC
AIR COOLER
H2O
AIR DRYERS
AIR TO STACK
P-510
P-511
KEY
KC SEQUENTIAL TIME CONTROL
ABSORPTION OF SO2
HEATING
COOLING
CATALYTIC, INC.
MOLECULAR SIEVE PROCESS FOR SO2 REMOVAL RECOVERY FROM SULFURIC ACID PLANT VENT GAS
W.A. PECK
NONE
ISSUED FOR COMMENT
42466
A-206
A

MOLECULAR SIEVE
TAIL GAS CLEANING SYSTEM P&ID

FIGURE 10

One advantage of this measurement system is the relative freedom from calibration changes caused by reduction in light transmission from dirty quartz windows or changes in the emission of light from the ultraviolet source. Only the signal difference represents the concentration of sulfur dioxide. The absolute values of light transmitted do not affect the output reading.

A proper sample system is essential and must be withdrawn to obtain accurate SO_2 readings of the stack gas. The sample point must be far enough downstream from the last piece of process equipment (eight stack diameters is required by the NSPS) to provide thorough mixing. The sample system must have appropriate filters to prevent solid material from collecting in the filter system. These filters must be changed regularly to prevent an accumulation of solids and a loss of flow.

Although the analyzer is insensitive to water vapor in the sample gas, excessive water vapor will cause an error in the sample flow rate measurement. To prevent condensation, the complete system must be heated from sample probe to analyzer.

Gas analyzing equipment requires careful and frequent service to ensure reliable and accurate reading. The analyzer must be zeroed and calibrated ever 24 hours using appropriate gases of known composition to ensure continued accuracy in the SO_2 reading. If recommended by the manufacturer, more frequent calibration should be made.

Most analyzers with automatic cycle control zero during each analysis cycle. This zero is often an electrical adjustment to change the recorder reading and does not substitute for the introduction of a zero SO_2 concentration gas. Air or nitrogen is often used for the zero calibration gas.

Calibration gases can be purchased from distributors equipped to mix gas to precise specifications. It is very important that the SO_2 concentration in calibration gas be checked periodically for consistency. The stack analysis using the standard EPA Method 8 can be run periodically and compared to the results obtained on the SO_2 analyzer. This confirmation will prove the satisfactory performance of the sample system and the analyzer.

The calibration and operation of the SO_2 analyzer must have a measurement error no greater than plus or minus 20 percent and a confidence level of 95 percent.

Continuous analysis of acid mist and opacity at the sulfuric acid vent stack is not required by the NSPS. However, when stack opacity reaches 10 percent or greater, without considering uncombined water vapor, a record must be maintained. Under potential failure of mist eliminator conditions and where acid mist emissions are suspected, an analysis should be run using EPA Standard Method 8. Details of this analysis can be found in the NSPS.

FACILITY RECORDKEEPING (Ref. 27)

Operators of sulfuric acid plants maintain operating logs, recording charts, and laboratory analysis sheets. Each plant determines the quantity and variety of information kept and the length of storage. The NSPS specifies the recording and maintenance of operating information pertaining to sulfur dioxide and acid mist emission control. The following summarizes a minimum of NSPS recordkeeping requirements:

1. A file will be maintained of monitoring and performance testing, quarterly excess emission reports, and all other reports and records required by NSPS.

2. Production rate and hours of operation are to be recorded daily. (See Table 3, for example.)

3. A record is to be maintained of the occurrence and duration of any startup, shutdown or malfunction in operation. (See Table 4.5 for example.)

Records are to be retained for two years. Items directly or indirectly associated with air pollutant emissions that should be recorded are indicated in Tables 4.1 to 4.5.

The inspector can review plant performance records by completing records during an inspection visit or by reviewing a checklist completed by facility personnel. The latter method appreciably reduces the time required of the inspector at each sulfuric acid production facility. The form presented in Table 9.1 in Section 7, can be completed in either manner.

FACILITY REPORTING (Ref. 26)

All reports and other communications to the Administrator are to be submitted in duplicate and addressed to the appropriate Regional Office of Environmental Protection Agency, to the attention of the Director, Enforcement Division.

The minimum written reports required from the operator are:

1. Notification of anticipated date of initial startup of new sulfuric acid plants, 30 to 60 days prior to anticipated startup date.

2. Notification of initial startup date, within 15 days after startup.

3. Results of performance tests. These tests are to be made within 60 days after achieving maximum production rate but not later than 180 days after initial startup. The owner or operator of an affected facility shall provide the Administrator 30 days prior notice of the performance test to afford the Administrator the opportunity to have an observer present.

4. A written report of excess emissions for each calendar quarter. The report is due on the 30th day of the month following the end of the quarter. A quarterly report is not required if no excess emissions occurred.

A report of excess emissions should include:

1. Magnitude of excess emissions measured by monitoring equipment and reduced to units of the standard.
2. Date of excess emission.
3. Time excess emissions started.
4. Time emissions returned to NSPS limits.
5. Nature and cause of any malfunction.
6. Corrective action taken.
7. Preventive measures adopted.

Table 3

DAILY PRODUCTION - 100% SULFURIC ACID

DATE	TIME START	TIME SHUTDOWN	OPERATING HOURS	PRODUCTION - 100% SULFURIC			
				LBS./HR.	TONS/HR.	METRIC TONS/HR.	TOTAL TONS

Table 4.1

NSPS DAILY RECORDKEEPING DATA SHEETS
SULFURIC ACID PLANT

Company Name ______________________ **Company Plant Code** ______________________

Plant Identification ______________________ **For Week Ending** ______________________

Plant Location ______________________

Part I of V, Process Data

DATE								**WEEK AVG.**
Item								
Hours Operated								
Feed Rate:								
Air, SCFH								
SO_2 SCFH								
Process Water, gpm								
Production Rate:								
Tons/Hr., H_2SO_4 (100%)								
Acid Strength, %								
Sulfur Conversion Efficiency, %								

Table 4.2

NSPS DAILY RECORDKEEPING DATA SHEETS

SULFURIC ACID PLANT

Part II of V, Emissions

DATE	NSPS STANDARD							WEEK AVG.
Item SO_2, ppm (by continuous monitor)	350 ppm or 2KG SO_2/ metric ton of 100% H_2SO_4							
Opacity, % (method 9) (unless 100% uncombined water)	10%							
lbs. SO_2/ton 100% H_2SO_4 (as SO_2)	4.0							
SO_3 Acid Mist	0.075 kg/MT or OO.15 lbs SO_3/1 ton							
NOTE: Daily averages to be weighed averages.								

Table 4.3
NSPS DAILY RECORDKEEPING DATA SHEETS
SULFURIC ACID PLANT

Part III of V, Emission Control Method

CHECK APPLICABLE METHOD	CONTROL METHOD	DESIGN SPECIFICATION	PERFORMANCE LIST EFFICIENCY; %
	Dual Absorption Alkaline Scrubbing Molecular Sieves Absorption		

DATE	NSPS							WEEK AVG.
Item								
Time in operation, hrs.								
Inlet conc., ppm SO_2								
Outlet conc., ppm SO_2								
SO_2 Reduction, %	99.7%							

Table 4.4
NSPS DAILY RECORDKEEPING DATA SHEETS
SULFURIC ACID PLANT

Part IV of V, Calibration and Maintenance

ITEM	DATE OR DATES	DESCRIPTION OF CALIBRATION AND MAINTENANCE
SO_2 Monitor		
Acid Flow (Abptn) Controller		
Process Water Flow Control		
Production Acid Flow Indicator, gpm		
Control Device		
Others:		

Table 4.5
NSPS DAILY RECORDKEEPING DATA SHEETS
SULFURIC ACID PLANT

Part V of V, Startup, Shutdown, and Malfunction History

Duration:

ITEM	DATE	TIME PERIOD	TOTAL TIME
Startup			
Shutdown			
Malfunction			

Detailed Explanation:

Corrective Action Taken:

Preventive Measures Taken:

SECTION 5

SHUTDOWN, STARTUP, AND MALFUNCTIONS

The pattern of malfunctions and shutdowns in sulfuric acid plants is difficult to establish because of the variation in plant condition, age and feedstock. A new plant can have one-half the shutdowns of an older plant and malfunctions causing excessive emissions of less severity and shorter duration. A plant using clean elemental sulfur feedstock can have fewer malfunctions and less frequent excess emissions than a plant using dark sulfur or reclaimed acid.

An evaluation of the excess emissions will include a review of plant operating records to determine the frequency and reasons for shutdowns. A high occurrence of excess emissions may require a review of operating and maintenance procedures, general plant condition, or feed, Tables 5 and 6.

SHUTDOWN (Ref. 1)

When a sulfuric acid plant is shut down, the emissions will not necessarily rise above those produced by the malfunction that made the shutdown necessary. The effectiveness of the shutdown procedure will be reflected in the emissions during the plant startup.

Planned Shutdown

The shutdown procedure used will depend on the purpose and the work to be done during the shutdown. The initial steps will be the same for each type. These are:

1. Have available a supply of strong acid to be transferred into the drying and absorption systems when excessive dilution occurs.

This addition of strong acid will help reduce acid mist emissions during the startup. Increase acid concentration in the drying and absorbing towers to help offset moisture leakage and dilution of absorbing acid.

2. Shut off sulfur flow and continue air flow through the sulfur furnace.

3. Continue air flow through the furnace, converter, and absorber for a short period until all sulfur dioxide is removed from the furnace and sulfur trioxide is removed from the converter to the absorber.

Unplanned Shutdowns

The emissions during an unplanned shutdown are produced by the malfunction that caused the shutdown. If a proper shutdown procedure cannot be followed, sulfur dioxide and sulfur trioxide will not be purged from the system and excess emissions will probably occur during startup.

STARTUP

A sulfuric acid plant can be restarted without excessive emissions if the temperatures in the catalyst beds of the converter and the temperature of the furnace have not dropped below an efficient operating level. If the temperature in the furnace and the converter have dropped below the minimum operating conditions, then the plant will require reheating before sulfur dioxide can be introduced into the converter. Otherwise, excessive SO_2 emissions will occur. A plant restarted without preheat will emit SO_2 in proportion to the length of time the plant has been shut down.

During startup, most plants will reach a peak SO_2 concentration in the vent gas approximately two hours after introduction of sulfur to the furnace.

By using proper startup procedures, the SO_2 emission concentration should drop to compliance level within four hours.*

When a new plant has been charged with new catalyst, a startup will require one to two days of slowly increasing production rates until full production is reached. Plants with catalyst exposed to moisture can be in full production without emissions in 3-4 days.

More details of shutdown, startup, and malfunction operations involving emissions will be found in "Evaluation of Emissions During Start-up, Shutdown, Malfunction and Normal Operating Conditions of Sulfuric Acid Plants" Task 6 Report of Contract No. 68-02-1322, EPA-600/2-76-010.

MALFUNCTIONS

Plant malfunctions causing excessive SO_2 and acid mist emissions can be grouped by the process in which they occur as shown in Appendix F.

Sulfur Feed System

Malfunctions in the sulfur feed system usually cause the reduction or stoppage of flow to the furnace and a reduction of SO_2 feed to the converter. Loss of sulfur feed to the furnace can be caused by plugging of the sulfur guns, trip out of the sulfur burner pumps, or loss of heat to the sulfur melting system. The loss of sulfur feed to the furnace will not produce excessive SO_2 emissions if the flow can be reinstated before the converter temperatures have dropped below the permissible operating range. If converter temperatures have dropped below this permissible range, high emissions of SO_2 may occur until temperatures are stabilized at the control points. Acid mist emissions can be caused in the sulfur feed system when steam (for jacketing) leaks into the sulfur feed pump, sulfur tranfer lines, and sulfur gun (burner). The system can produce acid emissions when excessive hydrocarbons, acid, ammonia, and halides are in the feed sulfur.

---

*NOTE - The acid concentration in the system cannot be increased substantially because of the narrow absorption range of SO_3 in sulfuric acid in the absorption tower(s). The range is usually 98.5 to 98.8%, and bad absorption of SO_3 occurs outside of this narrow range.

Combustion Air

Insufficient combustion air to the furnace or dilution air to the converter is one of the most frequent causes of excessive SO_2 emissions. Excessive wear, or errosion of the blower blades, will cause decreased air flow after many years of operation. The clearances of the impeller blades and the casing must be checked periodically to ensure full flow of air.

Malfunctions of Blower

The air blower unit normally is driven by a steam turbine. A reduction in blower speed, or other malfunction causing a reduction in air flow, will result in incomplete conversion of sulfur dioxide to sulfur trioxide in the converter because of low oxygen/SO_2 ratio. Further reduction in air flow to the furnace will cause incomplete combustion of sulfur to sulfur dioxide. The unburned sulfur may sublime and redeposit in the catalyst beds. When proper air flow is restored, excess sulfur dioxide will be produced by oxidation of this sulfur in the catalyst bed. This excess will overload the converter and produce excess sulfur dioxide emissions.

Sublimation in the furnace may cause sulfur to be deposited and burned in the boiler tubes and cause tube failure. Sulfur deposition on catalyst will destroy the catalyst by reducing the activity porosity and the conversion activity. Sublimed and recondensed sulfur can also plug heat exchangers, demister, media, towers, and even the acid distributor systems. A sudden failure of the air blower causing a plant shutdown will not permit the sulfur dioxide and sulfur trioxide to be swept out of the system. These gases will cause excessive emissions from the plant during the startup.

Malfunction of Air Drying Tower

Too high acid concentration can cause acid mist carryover into the furnace. Moist air feed to the plant can be caused by a low concentration of acid in the drying tower or a reduction of acid flow. Wet air feed to the acid plant usually is indicated by a heavy white plume of acid mist from the vent stack. The white plume and acid emission will continue until the plant is shut down or concentration and flow of the drying acid is restored.

Plugging of the tower packing can occur from sulfate, dirt from the air, and from sublimed/recondensed sulfur. This plugging can cause improper drying of the air and lead to acid mist problems.

Errosion of acid distributors (weirs or parts) can cause improper distribution in the packing and lead to acid mist problems caused by improper drying.

Heat Exchangers, Boiler, Superheaters, Economizers

Sulfuric acid plants are equipped with gas to liquid heat exchangers and gas to gas heat exchangers. The most common malfunction occurring with heat exchangers is leaks allowing water or steam to enter the process streams and producing a dense white plume at the vent stack. Leaks to gas heat exchangers used in dual absorption plants can allow bypassing around the converter and excess sulfur dioxide emissions.

CONVERTER

The most common cause of sulfur dioxide excess emissions is loss of temperature control in the converter. Sulfuric acid plants may use automatic control or manually adjusted dampers for establishing temperatures within the acceptable range. It is estimated that some temperature control problems will arise on an average of one time in each 24-hour period. If the converter temperatures deviate from the normal setpoint by more than one to two percent, inefficient conversion to SO_3 will occur. Careful operator attention to the SO_2 analyzer in the vent stack should permit early detection and quick correction of these problems. Converter malfunctions can occur as a result of converter grates failing (breaking) and dumping the catalyst from the bed. This malfunction will cause gas bypassing and loss of conversion efficiency. Catalyst loss of activity can result from foreign material such as excess moisture, sulfur, halides, (fluorine, etc.), dust, etc. in the gas stream.

Mist Eliminator

Malfunction caused by errosion, shrinkage, or plugging can result in acid mist problems. Plugging can result from condensed sulfur, dirt in the air or feed sulfur, sulfate in the acid mist carryover, or sulfate dripping on these units from the tower's top, outlet elbows, or stacks.

Careful operator attention should permit early detection and quick correction of these problems.

Absorber and Strong Acid Systems

In a dual absorption plant the concentration of absorber acid feeding the primary and secondary absorbers can contribute to SO_2 and SO_3 emissions from the plant. Control system failure can produce high or low concentrations of acid in circulation. A failure to maintain proper acid circulation will produce acid concentration changes and an inefficient operation of the absorbers. Also, loss of temperature control will result in inefficient absorber operation. Plugging or improper distribution of acid can cause similar problems with the absorbers. Any deviation from the concentration flow or temperature range permissible for efficient SO_3 absorption will cause sulfur trioxide emissions and acid mist from the plant. High inlet gas temperatures to absorption or oleum towers will also produce acid mist plumes. If the problem occurs in the primary absorber, the SO_2 concentration in the vent also will increase since the efficiency will be reduced by the increased SO_3 concentration in the gas. Drastic changes of acid concentration or temperature control in any of the towers, and especially in the final absorber, will result in SO_3 emissions. Most commonly, failure of an acid circulating pump, loss of dilution water supply, or instrument malfunction causes these changes. Liquid sulfuric acid carryover can result from a plugged demister in the final absorber tower. Excessive flow rates through the absorber will also cause this type of acid mist emissions.

Sulfur Dioxide and Acid Mist Emission Control Systems

In a single absorption acid plant equipped with a tail gas cleaning system high emissions are caused by a malfunction in the cleaning system rather than in the acid plant. In the sodium and ammonium scrubbing systems, the most common causes of excess emissions are loss of solution concentration control, absorber solution pH control systems failure, loss of absorber solution circulation, and improper temperature control. These conditions can result from failure of circulating pumps, instrument failure, or improper operation of ammonia vaporizer.

Most ammonia scrubber systems are equipped with a sulfur recovery system that does not directly affect the operation. Failure in the recovery system should not cause emissions from the scrubber. The sodium scrubber system, however, depends upon recycled solution from the recovery system as makeup to the scrubber. Any plugging of the crystallizer-evaporator or failure of instrument or pumping systems causing a change in the concentration or flow of absorber solution cause high SO_2 emissions.

Malfunction of the sodium and ammonium scrubbing systems is caused by the operation of the scrubbers at a gas rate in excess of design conditions or with a scrubbing solution concentration below the required level.

Because of the simple design of the molecular sieve SO_2 adsorption system, most malfunctions will result from instrument failure or in cycle timer failures. Failure of the air blower will prevent regeneration of an SO_2 adsorber and cause high emissions when the unregenerated adsorber is automatically placed back in operation.

Table 5

EXCESSIVE SO_2 EMISSIONS INCIDENT

Date: ______________________ Time: ______________________

Shift: ______________________

Shift Foreman: ______________________

1. Maximum SO_2 level reached: ______________ ppm

2. Duration that SO_2 limit (300 ppm) was exceeded: ________ hours

________ minutes

3. Primary cause of upset: ______________________

____

____

4. Unit data

a) Furance temperature: ______________

b) Rate: ______________

c) Converter temperatures:

1st pass in ______________

1st pass out ______________

2nd pass out ______________

3rd pass in ______________

3rd pass out ______________

4th pass in ______________

4th pass out ______________

d) Acid strengths:

Interpass tower ______________

Final Tower ______________

e) Acid temperatures:

Interpass tower ______________

Final tower ______________

5. Additional information: ______________________

____

____

TABLE 5 (continued)

SHUTDOWN PLANNING CHECKLIST

Date -

Plants -

Foreman -

1. Reason for Shutdown - ______________________________

2. Will repairs require a total steam or water outage? If yes, list all checks that were made by operations and maintenance to ensure that a total outage is necessary for repairs - ______________________________

3. Has maintenance foreman been notified of possible shutdown? ________ Are needed materials or spare parts available? ______________________________

4. Has General Foreman been contacted? (After above steps have been taken)

5. What is the estimated time for repairs? Total time will include equipment repairs and operations shutdown and startup. (Break down into maintenance time and operating time). ______________________________

6. Have shift foremen from associated or dependent operations been notified of approximate time of shutdown and steam priorities?

____

____

____

7. After plant shutdown is completed, have all necessary safety procedures (valve tagging, tank entry checks, etc.) been followed?__________

____

____

____

8. Before plant startup, have all effected areas been notified?__________

____

____

STARTUP

1. When repairs have been completed and plants(s) are back on line, please fill out the following:

   A. Actual cause of equipment failure____________________

   ____

   ____

   B. Actual downtime? Explain any large amount of difference in actual and estimated downtime____________________

   ____

   ____

   ____

   C. Did we have any equipment that didn't operate or respond properly during startup? If so, have W.O.'s been written?____________________

   ____

   ____

____

General Foreman - Sulfuric Plant

Table 6
STARTUP, SHUTDOWN AND MALFUNCTION HISTORY

Date ____________________

☐ Startup — Time Start ____________________

☐ Shutdown — Time Stop ____________________

☐ Malfunction

SULFUR DIOXIDE

__________ ppm

__________ KG per metric ton

__________ lbs. per ton

Nature of Malfunction ____________________

____

____

____

Cause of Malfunction ____________________

____

____

____

Corrective Action Taken ____________________

____

____

____

Preventative Means Adopted ____________________

____

____

____

____

CAUSE OF TRANSIENT CONDITION	EFFECT ON PROCESS	CORRECTIVE ACTION	FREQUENCY OF OCCURRENCE	DURATION OF CONTROL	STACK EMISSIONS	PREVENTION OR CONTROL	COMMENTS	EXAMPLE *
Converter Bed Inlet Temperature Out Of Range Dual Absorption Plant	Conversion Efficiency Reduced	Manual Adjustment of Dampers, Adjustment or Repair of Instruments	Daily	2 Hrs.	SO_2, 400 - 1,000 PPM	Proper Operation and Control and Maintenance	Range of Permissible Variation From Temperature Specifications on Inlet Temperatures is 1 to 3% of Specified Temperature	Table 4A
Planned Shutdown Dual Absorption Plant SAP With Scrubber	Sulfur Feed Stopped and Unit Purged of SO_2 & SO_3	Manual Adjustment of Valves and Controllers	4/Yr to 1/2 Yr.	1 Hour to 2 weeks	None	Proper Procedure for Shutdown to Facilitate Startup	Planned Shutdown Should Not Cause Emissions On Shutdown. Proper Shutdown Minimizes Startup Emissions	Figure 21
Startup Dual Absorption Plant	Warm Plant After Short Term Shutdown (< 4 Hrs.)	Preheat of Plant Not Required	12/Yr.	4 Hrs.	< 300 PPM SO_2	Heat Conservation and Proper Startup Procedures	SO_2 Concentration Inlet to Converter Most Important to SO_2 Emission Control	Table 11 & 12
Startup Dual Absorption Plant	Cold Plant After Long Term Shutdown (> 4 Hrs.)	Plant Must Be Preheated Up to 5 Days	1-2 Times/Yr.	3-5 Days	< 300 PPM SO_2	Complete Preheat and Reduced SO_2 Inlet Conc. Startup Period 4-5 Days Using Proper Startup Procedure	SO_2 Concentration Can Be Kept Below NSPS With Sufficient Preheat Time End Low Initial Inlet SO_2 Concentrations. This is Ideal And Seldom Used Because of Production Loss During Long Startup. Auxiliary Preheaters Required for Faster Heat Up.	Figure 15
Startup Dual Absorption Plant	Cold Plant After Long Term Shutdown (> 4 Hrs.)	Plant Receives Minimum Heat Before SO_2 Addition	1-4 Times/Yr.	4-6 Hrs.	300 to 3000 PPM SO_2	Minimum Preheat is Applied and Inlet SO_2 Concentration is Started At Full Rate	Startup Method Most Commonly Used to Minimize Startup Time and Product Loss. Balance With Above Method Most Desirable	Table 11 Figure 12 & 16
Misoperation of Sodium and Ammonia Scrubber Systems	Operation at Gas Flow Above Design Limit	Operate Scrubber With Gas Flow Within Design	Daily	1-6 Hrs.	Up to 1,200 PPM SO_2	Reduce Gas Flow Rate. Proper Instruments and Procedures.	Most Common Cause of High SO_2 Emissions is High Gas Flow. More Conservative Design Should Be Employed.	Figure 22 & 23
Misoperation of Ammonia Scrubber Systems	High Gas Flow Rates and Solution Concentration Too Low	Reduce Gas Flow Rate and Increase Solution Concentration	Daily	1-6 Hrs.	Up to 1,200 PPM SO_2	Operate With Gas Flow Within Design and Solution Concentration At 7%. Proper Instruments and Procedures.	Operation With Solution Concentration at 4% (Specified Set Point) Will Reduce NH_3 Consumption But Will Produce High SO_2 Emissions.	Figure 20 & 22

* Ref. 1 - EPA-600/2-76-010

CAUSE OF TRANSIENT CONDITION	EFFECT ON PROCESS	CORRECTIVE ACTION	FREQUENCY OF OCCURRENCE	DURATION OF CONTROL	STACK EMISSIONS	PREVENTION OR CONTROL	COMMENTS	EXAMPLE *
Brink Filter On Ammonia Scrubber Outlet Inoperative	High Opacity and High SO_2 Readings On Reich Test	Restore Effective Operation of Brink Filter	1/2 Year	Continuous Until Repaired	SO_2 Reading Up to 3,000 PPM High Opacity	Repair Leak in Brink Filter Internals. Place Booster Blower and Brink in Service.	Brink Sometimes Bypassed on Startup Because of Lack of Steam for Booster Blower. Corrosion Can Cause Leak Around Filter Sleeve Connections.	Table 7 & 14
Loss of Sulfur Flow to Furnace	Low SO_2 Inlet Concentration	Restore Burner or Pump Operation or Unplug Burners	Frequent	1-4 Hours Depends Upon Operator	None	Use Clean Sulfur, Proper Sulfur System Maintenance and Operator Attention.	Loss of Sulfur Feed Will Not Cause High SO_2 Unless Extended Period Reduces Converter Temp.	Figure 23
High Sulfur Flow to Furnace	High SO_2 Inlet Concentration	Reduce Sulfur Flow to Furnace or Increase Air for Proper SO_2 Concentration	Frequent	Depends Upon Operator Attention	High SO_2	Control SO_2 Inlet Concentration Consistant with Catalyst Condition	Dual Absorption Plant Normally Uses Higher SO_2 Inlet Concentration Than Single Absorption. Catalyst Condition Limits Concentration.	Figure 23
Loss of Dilution Water to Primary Absorber	Increased Absorber and Concentration of Acid	Restore Dilution Water Flow to Pump Tank	Infrequent	Continuous Until Repaired	SO_2 Increased Small SO_3 and Opacity Increase	Assure Adequate Supply and Instrument, Maintenance Operator Inspection	Reduced SO_3 Absorption in Primary Absorber Increases SO_2 Exit Converter by Equilibrium Shift in Succeeding Converter Stages. SO_3 and Opacity May Be Increased.	Figure 23
Loss of Dilution Water to Secondary Absorber	Increased Absorber and Concentration of Acid	Restore Dilution Water Flow to Pump Tank	Infrequent	Continuous Until Repaired	SO_3 and Opacity Increased	Assure Adequate Supply and Instrument, Maintenance Operator Inspection	Secondary Absorber Will Increase SO_3 and Opacity But Will Not Increase SO_2 Emissions	Figure 23
Feed of Dark Sulfur or Sludge Acid	Increased Water in System	Change Feed, Filter Sulfur	----	Continuous Until Feed Change	Acid Mist Increased	Improved Demisters and Filters Such As Brink High Efficiency	Additional Water in System Causes Generation of Acid Mist. Modern Dual Absorption Plants Will Remove Most With Efficient Demisters.	Figure 17 & 19
Feed of Dark Sulfur or Sludge Acid	NO_x Generation in Furnace	Change Feed, Filter Sulfur	----	Continuous Until Feed Change	Acid Mist Increase	Improved Demisters and Filters Such As Brink High Efficiency. Use of ESP	Presence of NO_x in Gas Stream Causes Formation of Acid Mist By Gas Phase Reaction Through Combination With SO_2	----

* Ref. 1 - EPA-600/2-76-010

SECTION 6

PERFORMANCE TESTS

Federal regulations require a performance test for a new or modified acid plant within 180 days after plant startup.* The inspector is to observe process and control equipment operations to ensure the tests are conducted under correct operating conditions and proper test procedures are followed.

The purpose of the performance test is to determine if the emissions standards will be met while the plant is operating at full design capacity under normal conditions that create the maximum emission rate. Operating data for the process and control of the equipment should be recorded as a comparison basis for further plant inspection. A sample performance test checklist is given in Table 8 at the end of this section.

PRETEST PROCEDURES

Although the New Source Performance Standards stipulate the exact procedures for compliance, facility personnel may misunderstand or not be aware of certain parts of the regulations. The inspector is to arrange a meeting with plant personnel to review the standards, latest revisions, and procedures prior to the performance test.

The inspector is to ensure that plant management understands the performance tests are valid only while operating at representative performance. At this time all parties should agree on the parameters constituting "representative performance". The inspector is to determine which testing firm will perform the tests. If no representative of the firm attends the meeting, the firm should be contacted to ensure the tests are run in accordance with the regulations. The chief purpose of the meeting is to outline clearly the test and the required test procedures.

* Refer to Appendix A for detail performance tests.

PROCESS AND CONTROL EQUIPMENT OPERATING CONDITIONS

Process parameter values which must be established before the tests are conducted:

1. Sulfuric Acid Production Rate
2. Sulfur Feed Rate, Sulfur Analysis
3. Air Flow Rates, Furnace, Converter, etc.
4. Percent SO_2 in Furnace, Converter, etc.
5. Pressure Profile of the Entire Plant
6. Representative Flows, Temperatures, Pressures (into and out of all equipment, both process and utilities streams).

The emission data corresponding to the plant operation parameters will include stack emissions for sulfur dioxide, acid mist, and opacity. Process data recorded during the test will be used to determine the emission rates and must be measured with sufficient accuracy to justify the reported emission values.

Emission rates are based upon the number of tons of production of 100 percent acid per day. An acceptable method of measuring production rate must be available. Flow meters or storage tank level measurements are acceptable when properly confirmed by overall process material balances. If tank level measurements are used, arrangements must be made to isolate the tank from other production inputs or product outputs. If storage capacity is limited, this isolation may be a disadvantage. If a flow meter is available, the readings can be used for establishing the daily production rate. Appropriate calibration procedures must be followed and periodic tests must be run to prove accuracy. With either production rate, measurement method analysis must be performed on a periodic basis to permit calculation of production on 100 percent sulfuric acid basis.

The inspector is to review the files, inspect the plants, determine data to be collected, and establish that all sampling requirements and necessary instruments are available. Operating flows, pressures, and temperatures should be collected to provide a strong comparison base for future inspections. The inspector is to prepare checklists and log sheets to ensure that no useful operating or emission control data is overlooked.

The production rate expressed metric tons per hour of 100 percent sulfuric acid shall be determined and shall be confirmed by a material balance. The inspector must be sure that enough data is collected to provide a material balance.

Acid mist and sulfur dioxide emissions expressed in grams per metric ton of 100 percent H_2SO_4 shall be determined by dividing the emission rate in grams per hour by the acid production rate. The emission rate shall be determined by the equation grams per hour = Q x C where Q = volumetric flow rate of the gas in dry cubic meters at standard conditions per hour and C is acid mist or sulfur dioxide concentration in grams per dry cubic meters at standard conditions.

EMISSION TEST OBSERVATIONS

Concentrations of sulfur dioxide and acid mist are to be determined by EPA Standard Method 8, Determination of Sulfuric Acid Mist and Sulfur Dioxide Emissions from Stationary Sources.

In this test, a gas sample is extracted from a stack sampling point and acid mist is separated from sulfur dioxide. Both fractions are measured separately by the barium thorin titration.

The number of vent stack sample traverse points is determined by EPA Standard Method 1, Sample and Velocity Traverses for Stationary Sources. This procedure determines the number and location of traverse points required to extract a representative gas sample and velocity profile across the stack.

The velocity and volumetric flow rate are determined by EPA Standard Method 2, Determination of Stack Gas Velocity and Volumetric Flow Rate (type S Pitot tube).

Stack gas velocity is determined from the gas density and measurement of the velocity using a type S (Stauscheible of Reverse Type) Pitot tube at the traverse points established by Method 1.

Stack gas analysis will be made by EPA Standard Method 3, Gas Analysis for Carbon Dioxide, Excess Air, and Dry Molecular Weight. Gas is extracted from a sampling point and analyzed for its components using an Orsat analyzer.

Opacity determinations are to be made by a qualified observer using EPA Standard Method 9, Visual Determination of the Opacity of Emissions from Stationary Sources.

The inspector must be familiar with test methods, record all test data, and review procedures and calculations for compliance with regulations. A summary of test methods is given in Table 7. When outside firms are to perform the testing on contract, the inspector should be assured of their competence and provide sufficient supervision to produce accurate results.

PERFORMANCE TEST CHECK LIST

Before a performance test can be run the facilities must be inspected carefully to be sure all instruments, measuring elements, and sample points are provided and calibrated. Operating log and performance test checklists must be prepared in advance. Temperatures, pressures, composition, and flow rate data must be collected to permit calculation of complete material balances around the process.

Because of the variation in process equipment arrangement and instrumentation provided, a special performance test checklist must be prepared for each plant. The checklist should be similar to the sample shown in Table 8. Standard operating and special stack analysis log sheets and flow rate sheets in the plant operation should also be collected for the performance test period.

Table 7

SUMMARY OF TEST METHODS FOR NEW AND MODIFIED SULFURIC ACID PLANTS

POLLUTANT	SAMPLING METHOD	TOTAL SAMPLES		COMMENTS
		PER REPETITION	PER TEST	

Table 8

PERFORMANCE TEST CHECKLIST

Company Name ____________________

Source Code Number ____________________

Company Address ____________________

Name of Plant Contact ____________________

Unit Designation ____________________

Plant Design Capacity ____________________

Startup Date ____________________

Date Reach Design Production Rate ____________________

Performance Test Date ____________________

Feed

☐ Bright Sulfur

☐ Dark Sulfur

☐ Other ____________________

Composition ____________________

Production Rate ____________________

SECTION 7

INSPECTION PROCEDURES

Major inspection emphasis will be on checking facility records and emission monitors to show how effective emission control has been since the last inspection. Records will show the current emission levels and can be used to evaluate the accuracy of the instrument and the effectiveness of the maintenance program.

In contact sulfuric acid plants, all the sulfur dioxide and the acid mist should discharge from the final absorption tower or the emission control equipment. However, fugitive emissions of SO_2 and acid mist from leaks in the process equipment are an important possible source of air pollution and must be included in the inspection.

INSPECTION POINTS - SULFURIC ACID MANUFACTURING

The inspection of sulfuric acid plants must take into account the interconnected, continuous nature of the manufacturing process, since there is one point of emission (in exit stack gases) for the major potential air contaminants. Windblown sulfur, sulfur dioxide, hydrogen sulfide, sulfuric acid mist, and nitrogen oxides arising from the manufacturing process will be emitted from the final absorption tower or from the control equipment following the tower.

The emission potential is dependent upon the type of process, age of the plant, whether or not oleum is produced, nature of the raw material, production rate, operating variables, and type of control equipment.

The major tasks the inspector performs include: (1) determination of the nature of the process as it affects air contaminant emissions, (2) examination of operating conditions and relevant records, (3) surveillance for plume appearance (if any), (4) determination of contaminant emission rates, and (5) investigation of possible property damage.

Inspection of the Premises

a. Interview

Most of the important information obtained in a sulfuric acid plant inspection will be from the interview with the plant management. The continuous enclosed nature of the manufacturing process precludes obtaining extensive information by visual inspection.

The inspector will wish to learn the specific details of the process employed, such as the nature of the sulfur source and the range in composition and extent of contaminants present. Even in a sulfur burning plant the latter item can be important. The rated capacity and normal operating rate of the plant should be obtained. Information on startup procedures and the frequency of shutdowns and startups is desirable. The nature of control and operating procedures and equipment should be secured. Items of importance are SO_2 and 0_2 concentrations entering the converter, temperatures at various points in the converter and absorption tower, and the concentration and temperature of the absorption tower acid. The inspector may be given the opportunity of examining operating records.

The inspector should obtain information on the efficiency of sulfur dioxide conversion and any collection equipment used and data on the tail gas composition finally being discharged to the atmosphere. He should inquire about maintenance procedures and frequency. (Ref. 28)

b. Physical Inspection

The inspector should become familiar with the physical layout of the plant. Usually the permit application files will contain most of the plant background data, flow sheets and drawings.

OUTSIDE OBSERVATIONS

Note plume opacity and color. Opacity of 10 percent or greater is in violation unless caused by presence of uncombined water only. Inspect the process equipment for gas and liquid leaks contributing to fugitive emissions and enter in Table 9.1.

Environmental Surveillance

The only visual evidence of emissions from the contact process for sulfuric acid manufacture is the white plume having a particle size range generally less than three microns. Particles larger than this do not scatter light in the visual wave length range effectively and thus may be present but not visible.

EMISSION MONITORS

The inspector is to observe a calibration and zero check of the sulfur dioxide stack monitor. A review of the procedures, methods, and schedule of maintenance will indicate compliance with the regulations and provide an appraisal of the validity of recorder emission data. A record of instrument maintenance and calibration should be made by completing Table 9.2, if not previously completed.

The sulfur storage area should be inspected to determine the potential for wind-blown sulfur dust losses. The inspector should investigate the possibility of hydrogen sulfide formation from molten sulfur containing hydrocarbon impurities.

Depending upon the type and age of the plant, indicating and/or recording instrumentation such as the following may be employed.

- Temperature (process gas entering and leaving the several converter stages and absorption towers).
- Acid concentration (drying tower and absorption towers).
- SO_2 concentration (entering the converter, entering and leaving the

absorption tower or tail gas scrubber).

Miscellaneous flow and pressure measurements.

Tests for sulfur dioxide, oxygen, acid mist concentration, and nitrogen oxides often can be performed manually.

The inspector should determine the capability of the plant to meet emission control regulations or the discharge of (1) sulfur dioxide in the effluent in excess of four pounds per ton of acid produced (two kgm per metric ton), maximum two-hour average, (2) acid mist in the effluent in excess of 0.15 pounds per ton of acid produced (0.075 kgm per metric ton), and (3) a visible emission. In determining compliance, the inspector should:

1. Check the number of catalyst stages - older plants that have only two stages typically have only 90-95 percent conversion of sulfur dioxide to sulfur trioxide. Plants with three stages of catalyst will typically have a 96-98 percent conversion of sulfur dioxide to sulfur trioxide. These conversion efficiencies are equivalent to emission rates of 26 to 52 pounds per ton of acid produced.

2. Determine types of acid mist eliminators (Table 9.3). Mesh mist eliminators with double pads will collect efficiently acid spray and mist from a properly operated 98 percent acid absorber. Teflon mist eliminators or high energy scrubbers are used to collect acid mist less than three microns in size to meet an emission limit of .15 pound per ton of acid, maximum two-hour average, expressed as H_2SO_4 or a visible emission.

3. Control room operating log. (Table 11)

   a. Check concentration of sulfur dioxide entering and leaving the converter. Any unconverted sulfur dioxide will pass through the absorber to atmosphere.

    b. Check temperature of 98 percent absorber tower acid. If the acid temperature is considerably above 180°F, excess sulfur trioxide and acid mist can be discharged to atmosphere.

    c. Determine operating rates from log and compare with design capacity from permit system records. Operation at over capacity can result in excessive emissions of sulfur dioxide and acid mist.

4. Source of potential nuisance problem:

    a. Effects of sulfur dioxide and acid mist on people and property.

    b. Excessive emissions of sulfur dioxide during cold startups, upset conditions or overload operations.

    c. Excessive emissions of acid mist during oleum production or improper operation of absorber.

Acid Mist Elimination (Table 9.3)

A special source of sulfur compound pollution is the acid mist which may be discharged to the atmosphere from the absorbers or dryers in a sulfuric acid plant. The Federal Emission Regulations limit this to 0.15 lb. per ton of acid produced, maximum 2-hour average, expressed as H_2SO_4. For a 1000 ton/day acid plant, discharging 74,000 cu. ft./min. of air at 190°F, this limitation corresponds to about 0.84 mg./std. cu. ft. The particle size in such a mist is very fine, running as much as 60 percent less than 3 microns.

The collection of acid mist has been successfully carried out by the use of fiber filter elements.

The inspector should attempt to relate tail gas concentrations and appearance to operating parameters. This information will be useful in interpreting causes of upsets or off-normal conditions leading to excessive discharge of air contaminants. It will be useful for the inspector to be present during a startup operation to obtain first-hand information on optimum procedures for minimizing losses. (Ref. 1 and 28)

Sulfuric Acid Mist Control (Table 9.3)

As can be seen from earlier portions of this section, acid mist emissions range from 2-20 mg/SCF (70-700 mg/M^3) for most of the sulfuric acid plants operating in the United States. Although sulfuric acid mist accounts for a relatively small proportion of the total sulfur losses (approximately 1-10%), it is responsible for visible plumes and is associated with material damage and health effects at lower concentrations than is sulfur dioxide.

Operational and process factors which affect acid mist emissions are:

- Improper concentration and temperature of the absorbing acid.
- Amount and concentration of oleum produced.
- High content of organic matter in the raw materials of a sulfur burning plant.
- High moisture content of the sulfur dioxide entering the converter.
- Stack cooling of sulfur trioxide gases leaving the converter, i.e., sudden cooling below the acid dewpoint, resulting in condensation of very small particles.
- Presence of nitrogen oxides, which can result from excessive temperatures in the sulfur combustion chamber, from nitrogen in raw materials, and from arcing in electrical precipitators.
- Insufficient acid circulation and lack of uniformity of acid distribution in the absorption tower.
- Improper type or dirty packing in the 98 percent absorber.

Many sulfuric acid plants utilize some form of collection equipment designed specifically for acid mist. The most common type is the two-stage knitted wire or Teflon mesh pad. Such pads operate at relatively low pressure drop (2-3" H_2O) and are effective for acid mist particles greater than 3 microns in size. For particles less than 3 microns in diameter, the efficiency is much lower (15-30%). These smaller particles are responsible for visible plumes and may be carried for considerable distances.

Venturi scrubbers operating at a pressure drop of about 35-40" H_2O have been used on acid concentrators where most of the acid mist particles are $> 3\ \mu$ (microns) but recently have been proposed for combined use in removing SO_2 and acid mist. Such units would not be expected to be effective for mist removal from oleum plants.

The only devices capable of reducing all size ranges of acid mist to 0.1 mg/SCF are glass fiber filters and electrostatic precipitators. Glass fiber filters operate at about 8" H_2O pressure drop. Electrostatic precipitators operate at low pressure drops (about 1" H_2O) but are initially quite expensive. They are also rather large because of the low gas velocities necessary for efficient operation.

Table 9.3 summarizes the expected performance for the acid mist collectors.

EQUIPMENT (Table 10)

Emissions can be caused by malfunctions or improper conditions in the plant, misoperation, or equipment failures.* These causes can be evaluated by using log sheets of past operations, data taken from current plant operations, data from past performance tests, and plant design data. Table 9 is a checklist to be used for recording inspection data and as a reminder of items to be inspected. Operating data taken at each inspection will provide a reference and aid in determining trends in operating variables.

* Reference 1 and 2

Dual Absorption Acid Plant (Table 11)

Because of the complexity, the dual absorption acid plant may require more detailed inspection than other types. To aid in analyzing the cause of excess emissions, log sheets from such periods should be compared to performance tests and design data. Deviations may show the cause of excess emissions.

It is difficult for plant operating people to detect results of a slow drift in operating values. These trends can be detected by comparing data from operating log sheets to performance test data. Comparison of data taken at each routine inspection may also show a trend in operating parameters.

A probable cause of slow increases in emission levels in a dual absorption acid plant is a reduction of catalyst efficiency from accumulation of foreign material and loss of catalyst activity. (Ref. 1 contains details of description.)

To determine any changes, catalyst conversion efficiency and acid production rates should be compared with data since the initial startup of the plant.

Plant operating people often slowly change the points on some process variable. This requires periodic checks to re-establish the operating points. These deviations can be determined by comparing operating logs to performance test data and observing current process controller setpoints.

A drift in the inlet temperatures to the catalytic converter beds will cause high SO_2 emissions. High SO_2 emissions can be caused by sudden process changes in the primary absorber flow rates, reducing absorption efficiency. The concentration of the primary absorber acid should be checked when SO_2 excess emissions occur.

Acid mist emissions can be caused by failure to maintain the concentration of the air dryer acid or the primary absorber acid at the proper value. However, the most likely cause of acid mist emissions from a dual absorption acid plant is plugging or corrosion of the acid mist entrainment separators. A comparison of pressure drop across these separators will show an increase if the separator is plugged, or a decrease in pressure drop of the separator is caused bypassing leaks.

The critical process parameters to be checked in the dual absorption plant are the catalyst bed temperatures and the absorber acid concentration.

SODIUM SCRUBBER PROCESSES (Table 12.1)

Acid Mist Scrubber

Acid mist that is not removed from the gas stream will flow through the sodium scrubber and will be emitted with the vent gas.

Process operating log sheets should be scanned for deviation from normal levels. During times of recorded excess emissions, the process parameters from these log sheets should be compared with performance test data to determine the cause.

The most important process parameter to check in this system is the differential pressure across the acid mist scrubber.

Sodium Scrubber (Tables 12.1 and 12.2)

The most critical part is the SO_2 absorber. Operating log sheets and charts from the absorber unit should be reviewed and deviations noted. Slow drifts in solution concentration or liquid/gas ratio should be noted. The deviations in process parameters at the time of excessive SO_2 emissions should be investigated to determine the cause, if possible.

Appropriate information should be entered in the inspection checklist for future reference including solution concentration and gas flow rate. (Tables 12.1, 12.2 and 12.3)

Recovery System

Although operation of the SO_2 absorber is the key to the sodium scrubber system, malfunctions in the recovery system can also affect the SO_2 removal efficiency and cause high emissions. Upsets or drifts in process parameters shown on the operating log sheets should be noted and the effect on absorber efficiency evaluated.

The inspection checklist will include the current concentration of the make-up solution returning to the scrubber. This is the most critical process parameter for the recovery system.

Ammonia Scrubber System (Tables 12.1 and 12.2)

Because most ammonia scrubber systems use a once-through system rather than a recovery process, it is likely to be influenced by problems in the recovery system than with the sodium scrubber. Operation of the ammonia scrubber system, however, is probably more sensitive to process variations than the sodium system.

Because of the sensitivity to some process parameters, deviations should be noted by comparison to performance test data. Periods of high SO_2 emission should be evaluated to determine the cause. Acid mist emissions should not be a problem unless caused by leakage of the mist eliminator or improper operation of the Venturi scrubber. When high plume opacity occurs, pressure drop across the filter or Venturi should be compared with the design data. An unusually high or low pressure drop may indicate the filter is becoming plugged, or has corroded and is allowing gas to bypass. An unusually low pressure drop across a Venturi scrubber indicates low efficiency operation resulting from a faulty scrubber or low gas or liquid flow rate.

High SO_2 emissions can occur from improper ammonia concentration or excess gas flow through the absorber. In times of SO_2 emissions, these values should be checked against performance test data to be sure operating setpoints have not drifted from the initial value or that instruments are not malfunctioning.

The inspection checklist should include ammonia concentration and gas flow.

Molecular Sieve Adsorption System (Table 13)

The molecular sieve adsorption system is simple to operate. Failure to meet SO_2 emission standards probably will be caused by degeneration of the material in the adsorber. The highest SO_2 emissions occur at the end of the adsorption cycle just before the tower is switched to regeneration. Records should be checked to determine any trend in peak SO_2 concentrations and cycle timer settings compared to performance test data. SO_2 emissions concentration higher than normal in the same cycle time could be caused by degeneration of the molecular sieve or increased SO_2 load on the adsorber.

High SO_2 concentration in the regeneration gas, low temperature or low air flow result in improper regeneration. These parameters should be checked on past operating logs and compared to performance test data to assure proper operation of the system and the equipment. Recordings from the water totalizer on the regeneration air dryer should be checked to determine the drying efficiency.

The recording charts of SO_2 emission during the adsorption and desorption cycles and of water concentration in the air during regeneration cycles should provide a good operation description. The inspection checklist should include regenerating air temperature and air flow.

Electrostatic Precipitators (ESP) (Tables 14 and 15)

Only a small number of modern sulfuric acid plants are equipped with electrostatic precipitators to remove acid mist from the process stream. Records should be checked for periods of high acid mist or high opacity emissions and operating data on the ESP analyzed to determine the cause. The electrostatic precipitators are subject to frequent failure. Maintenance records will provide an indication of the overall operating quality of the unit. Many times low voltage (EMF) in ESP will cause malfunctions and plume problems.

The inspection checklist for ESP should include secondary current, voltage and spark rate.

INSPECTION CHECKLIST

Each inspection of a sulfuric acid plant should provide sufficient checklist data as a record of the operation during the life of the unit from performance test through shutdown. Trends recorded in these checklists provide information for evaluating condition of the plant, skill of operation, and quality of maintenance. The inspection checklist in Table 11 contains most of the critical process parameters affecting emissions from sulfuric acid plants, but observation should be made on any unusual occurrence that might help explain emission problems.

Comments concerning the general conditions in the plant should be included in the checklist to point out fugitive emissions and to evaluate operation and maintenance quality. (Tables 15 and 16)

The inspection checklist should note an excessive number of shutdowns, startups in the plant, frequent changes in production rate, and significant changes in the quality of sulfur feed.

INSPECTION RECORDS AND FOLLOW-UP PROCEDURES (Tables 16 and 17)

At least half of the inspection will be reviewing plant operating records. Emission monitoring records should be scanned and the occurrence of sulfur dioxide emissions noted. The standards for sulfur dioxide, acid mist, and opacity. are listed in Section 2. Space has been provided to record these incidents.

Gas monitoring instruments record concentrations in parts per million. Appendix B contains graphs for converting parts per million values to pounds per ton of 100 percent acid production. The sulfur dioxide concentration in the vent gas corresponding to four pounds of sulfur dioxide per ton of 100 percent sulfuric acid is 180 to 350 parts per million, depending on inlet SO_2 volume percent concentrations.

The records of the plant feed should be scanned for any change and acid production checked to determine if unit capacity was exceeded. Production rates should be recorded for periods of excessive emissions.

Maintenance methods and frequency should be reviewed. Review the records of startups, shutdowns and malfunctions, note the frequency, note action taken to alleviate future occurrences, and record in Table 12.3.

INSPECTION FOLLOW-UP PROCEDURE (Table 17)

With the information taken during the inspection a material balance can be made and from the emission data an evaluation of the standard can be made. This evaluation can be used to verify the testing results when submitted by the plant owner.

An inspection report must be prepared answering all of the questions of why, who, what, when, where, and how (as shown in Table 17). If this is the first performance test, there is no past data. However, when later inspections are made the prior performance records will provide a better picture of the operation practices.

Follow-up inspections shall be made about every three months, unless the plant emissions require more or less frequent inspections.

Copies of the inspection report should be sent to the Regional Office, State Agency, and plant owner.

ENFORCEMENT PROCEDURE (Table 17)

The objective of operation inspections is to establish compliance with particulate emission regulations. In order to accomplish the above objectives, the enforcement official needs to determine:

1. Current production levels and operating conditions.
2. Design production levels and operating conditions.

3. Current controlled and uncontrolled particulate emission levels of SO_3 acid mists and SO_2 emissions levels.

4. Efficiency and adequacy of emission control equipment at current and design operating levels.

Emission control equipment design capacities and operating conditions can be obtained from design drawings and plans. These data should be obtained from the company representative prior to physical plant inspection. Production levels and emission control equipment operating conditions are monitored by the plant operator and are recorded in the operator's daily log or are displayed on instrument panels (Table 18).

The plant will have a control booth near the units for monitoring. The enforcement official should have little difficulty assessing the current operating status of the vessels by observing the many recorders, gages and log sheets.

Emissions from an installation depend on the operating condition of the control equipment. Part of this manual provides detailed analysis of the air pollution control devices.

The enforcement official should observe one complete shift. Certain types of operational data should be recorded on the inspector's worksheets. If possible, this data should be compared to other plant records for other shifts to diagnose whether there are any unusual temperatures, especially with respect to capacity and SO_2 flow rate. Table 18 is an example of the kind of operating logs that are commonly used.

The enforcement official should complete all inspector's worksheets for contact acid plants. The data on each sheet can be used as a comparison of the operating variables from inspection to inspection. As usual, the enforcement official should verify that the ducts, fans, and abatement equipment are maintained regularly and are functioning properly.

It is not only important that the control equipment be operating correctly during the inspector's visit, but operating continuously. The routine maintenance of control equipment should be verified as for effective air pollution control. It is mandatory that plant operators carry out a regular maintenance program.

Since air pollution emissions depend primarily on the abatement equipment, the enforcement official should spend most of this time assessing the operating condition of the air pollution control devices.

Visible emissions are the simplest means for estimating particulate control-equipment performance, and the enforcement official should estimate the percent opacity of control equipment stack plumes. If in excess of allowable limits, appropriate action should be taken.

Building openings should be observed for evidence of escape of inadequately captured process fumes and, if so noted, determine point(s) of origin and require corrective actions.

Table 9.1

NSPS INSPECTION CHECKLIST FOR CONTACT ACID PLANTS
PERFORMANCE TEST

Company Name ____________________
Source Code Number ____________________
Company Address ____________________
Name of Plant Contact ____________________
Unit Designation - Identification ____________________
Plant Design Capacity ____________________
Actual Present Capacity ____________________
Previous Inspection Date ____________________
Present Inspection Date ____________________

A. Pre-Entry Visual Observations   Time __________ Date __________

Weather Conditions ____________________
Stack Plume Color ____________________

Equivalent Opacity (circle one):
0 10 20 30 40 50 75

Opacity Regulation ☐ in compliance
☐ not in compliance

Note vapor or gas leaks off dry equipment ____________________
Note fugitive dust or liquid emissions ____________________
Is SO_2 odor present?__________Strong, Detectable, Barely detectable __________

B. Emission Monitors   Time ____________________

Concentrations	Transmittance Opacity	or	__________	% lbs/ton 100% H_2SO_4	
	Sulfur Dioxide		__________	ppm	__________lbs/ton
	Acid Mist		__________	ppm	__________lbs/ton

Calibration	Gas conc. (ppm)	Gas pressure (psig)	Monitor readout (ppm)	Statis.	Unsat.
SO_2	________	________	________	☐	☐
Acid Mist	________	________	________		

Describe Ductwork Condition, Corrosion, Leaks ____________________
Maintenance Program ____________________

Table 9.2

SULFUR DIOXIDE MONITOR
CALIBRATION, ZERO ADJUSTMENT AND MAINTENANCE

DATE	DESCRIPTION OF CALIBRATION OR MAINTENANCE

Table 9.3 EXPECTED PERFORMANCE OF ACID MIST COLLECTION SYSTEMS

System	Efficiency >3 Microns	Efficiency <3 Microns	Emission Level 99% Acid Plants	Emission Level Oleum Plants
Wire or Teflon Mesh	99+%	15-30%	to 2 mg/SCF	to 5 mg/SCF
Glass Fiber Filter	100%	95-99%	0.1 mg/SCF	0.1 mg/SCF
Electrostatic Precipitator	99%	100%	0.5 mg/SCF	0.1 mg/SCF
Venturi Scrubber	98%	Low	3 mg/SCF	Ineffective with <3 micron mist

Unless additional control equipment is used, the tail gases leaving the absorption tower are discharged to the atmosphere. Typical tail gas concentrations from a 4-stage sulfur burning contact acid plant are shown below:

SO_2	1500-4000 ppm
Acid Mist	2-20 mg./SCF
SO_3	0.1-1.3 ppm

Table 10

PREINSPECTION DATA SHEET

☐ Adequate Information

☐ Inadequate Information (Obtain needed data during first inspection)

SLUDGE ACID

FIRING CAPACITY PER BURNER
Rated ______________ Btu/hr
Normal ______________ Btu/hr
Maximum ______________ Btu/hr

WAS UNIT A CONVERSION UNIT ☐ YES ☐ NO

IF GAS STANDBY, STATUS OF BURNER
☐ Left in Firebox
☐ Pulled Out and Stored
☐ Multiple Fuel Burner

CONTROL EQUIPMENT
Type of Cleaning Equipment ______________________________
Pressure Drop Across Collector ______________ in H_2O
Design Efficiency (if known) ______________ %
Airflow to Control Device Inlet ______________ ACFM @ ______________ °F
Stack Diameter ______________ ft
Stack Height ______________ ft
Stack Temperature ______________ °F

MONITORING	YES	NO
Opacity Meter	☐	☐
Others	☐	☐
SO_2 Meter	☐	☐
SO_3	☐	☐
O_2 Meter	☐	☐
CO_2 Meter	☐	☐
Combustion Gas Analyzer	☐	☐
SO_2 Alarm	☐	☐

MAINTENANCE AND OPERATING RECORDS KEPT	YES	NO
Amount of Steam Generated	☐	☐
Amount of Sulfur Used	☐	☐
Type of Burner Used	☐	☐
Sulfur Burner Equipment	☐	☐
Instrumentation Calibration	☐	☐
Fans, Ductwork, Control Equipment	☐	☐

Table 11
Typical Operating Reading Data Sheet for Sulfuric Plants

	Set Points	2-19	2-20	Ave.	Min.	Max.							
SULFUR SYSTEM PRODUCTION		1600	1600	1600	1600	1850							
Pit Temperature - $^{\circ}$F		266	267	266	260	270							
Pit Level - Inches		52	52	--	--	--							
BLOWER - FLOW RATE, SCFM				100, 776	92, 262	106, 593							
Suction - H_2O		4.4	4.2	4.3	4.2								
Discharge - H_2O		195	185	190	183	201							
Speed - RPM		3500	3330	3467	3310	3600							
BOILER													
Steam Pressure - PSIG		490	490	500	490	600							
Water Level - Inches		0	0	--	--	--							
Cont. Blowdown Valve Setting		0	0	--	--	--							
GAS TEMPERATURES - $^{\circ}$F													
Gas Lvg. Sulfur Burner	750°F	1715	1746	1717	1690	1750							
Gas Lvg. No. 1 Boiler		735	721	--	--	--							
Gas Lvg. No. 2 Boiler		735	719	--	--	--							
Gas in No. 1 Converter Mass	820°F	805	1740	801	795	806		800–850°F			425–455°C		
Gas Lvg. No. 1 Converter Mass		1118	795	1111	1097	1118		1100–1150°F			595–620		
Gas in No. 2 Converter Mass	800°F	845	1098	840	826	846		800–850°			425–455°		
Gas Lvg. No. 2 Converter Mass		992	828	994	988	1001		950–1000°			510–540°		
Gas in No. 3 Converter Mass	800°F	822	1000	823	816	832		800–850°			425–455		
Gas Lvg. No. 3 Converter Mass	790°F	821	886	869	859	886		875–925			465–495		
Gas in No. 4 Converter Mass (1st Layer)		863	832	824	815	834		780–810			415–432		
Gas in No. 4 Converter Mass (2nd Layer)		821	832	851	842	866					418–435		
Gas Lvg. No. 4 Converter Mass		846	864	851	852	866		785–815					
INTERPASS ABSORBING ACID, EXIT GAS TEMPERATURE $^{\circ}$F	200°F												
Temperature Acid to Tower $^{\circ}$F	160°F	150	184	185	150	185							
Pump Tank Level - Inches Acid		42	42	--	--	--							
Dilution Water - GPM		44	44	--	--	--							
Acid Strength - % H_2SO_4	98.6	98.5	98.8	98.6	98.5	98.9							
Acid Flow to Tower - GPM		4000	4000										
FINAL ABSORBING ACID SYSTEM INLET GAS TEMPERATURE $^{\circ}$F	190°F												
Temperature Acid to Tower - $^{\circ}$F	160°F	179	175	160°	160°	185°							
Dilution Water - GPM	--	420	--	--	--	--							
Acid Strength - % H_2SO_4	98.6	98.5	98.6	98.6	98.5	98.9							
Acid Flow to Tower - GPM		2320	2340	--	--	--							
Acid Flow to Sales/Storage GPM													
DRYING ACID SYSTEM													
Temperature Acid to Tower - $^{\circ}$F	160°F	112	111	160°	160°	185°							
Pump Tank Level - Inches Acid		--	43	--	--	--							
Dilution Water - GPM		4.0	120	--	--	--							
Acid Strength - $^{\circ}$Be or % H_2SO_4	98.6	94.62	93.38	98.6	98.5	98.9							
Acid Flow to Tower - GPM		2300	1850	--	--	--							
Exit Gas Temperature $^{\circ}$F													
GAS ANALYSIS													
% SO_2 Int. Converter, Reich	8.8	8.7	8.8	8.0	8.0	8.9							
% SO_2 Exit Stack, Reich		.03	.03	.03	.01	0.04							
% SO_2 Exit Recorder/Monitor	300	= 130	110	120	50	385							
% Conversion	99.7+	99.7	99.7	99.83	99.75	99.86							
pH - Cooling Water	7.0	6.8	6.9	6.9	6.8	7.0							

Table 12.1

AIR POLLUTION CONTROL EQUIPMENT

Type

Mechanical – Mist Eliminators/Collectors Type ______________________

Interval Between Acid Drain Cleanouts ________ hours

Exterior Condition of Supports ☐ Satisfactory ☐ Unsatisfactory

Acid Level Indicators ☐ Satisfactory ☐ Unsatisfactory

Pressure before Collector __________ in. H_2O

Pressure after Collector __________ in. H_2O

Scrubber – Alkaline Absorbent ______________ pH Level ____________

Scrubbing liquor flow __________ GPM, Temp. ^oF ______ Concentration, ____ %

Pressure before scrubber __________ in. H_2O

Pressure after scrubber __________ in. H_2O

Gas Flow Rate ______________ SCFM

Pressure Drop ______________ in. H_2O

Removal of SO_2 Efficiency __________ %

Electrostatic Precipator

Interval Between Hopper Cleanouts __________ hours

Exterior Condition ☐ Satisfactory ☐ Unsatisfactory

Spark Rate: ______________ sparks/minute

Operating Voltage (KV)	Operating Current (MA)	
______________	______________	Field 1
______________	______________	Field 2
______________	______________	Field 3
______________	______________	Field 4

RECORDKEEPING REQUIREMENTS

Item	Number		
Sulfur burned	______________	Tons/day	daily record; maintain records for 3 months
Secondary temperature APC Device Design Parameter (Specify pressure drop, corona power, water flow rate, etc.)	______________		maintain recording charts for 3 months once per shift.

Table 12.2

CONTROL EQUIPMENT

Time ____________________

☐ Acid Mist Scrubber
☐ Sodium Scrubber
☐ Ammonia Scrubber

SECTION	1	2	3	4	PERFORM. TEST
Pressure Drop Across Scrubber (in H_2O)					
Tower Circ. Solution Temperature °F					
Solution Circ. Rate (GPM)					
Solution Conc. %					
Solution pH					
Make-Up From Recovery Conc. %					
Make-Up From Recovery pH					
Gas Flow Rate SCFM					

Table 12.3

INSPECTION CHECKLIST
SULFURIC ACID PLANT
EQUIPMENT MAINTENANCE

Plant Inspection

GENERAL HOUSEKEEPING

Below Average		Average		Above Average
☐	☐	☐	☐	☐

Comments: ______________________________

EQUIPMENT APPEARANCE

Below Average		Average		Above Average
☐	☐	☐	☐	☐

Comments: ______________________________

NOTE THERMAL INSULATION CONDITION

Below Average		Average		Above Average
☐	☐	☐	☐	☐

Comments: ______________________________

NOTE ACID LEAKS OBSERVED: Number ____________ Severity ____________

NOTE GAS LEAKS OBSERVED: Number ____________ Severity ____________

EQUIPMENT MAINTENANCE RECORDS

Preventive Maintenance Program Established ☐ Yes ☐ No

Is P.M. Program Being Followed ☐ Yes ☐ No

Number of P.M. Tasks Not Completed Last Month ________ /Previous Month ________

Number of Forced Shutdowns Last Month ________ /Previous Month ________

Percent Downtime for Maintenance Last Month ________ /Previous Month ________

Number of Occurrences of High Emissions Resulting from Equipment Malfunction Reported Last Quarter ______________________________

Critical Equipment Causing the Highest Frequency or Severity of Emissions (more than one occurence) ______________________ number ____________

Is P.M. Program Adequate ☐ Yes ☐ No

Table 13

☐ **Molecular Sieve**

SECTION	1	2	3	4	PERFORM. TEST
Pressure Drop Across Tower (in H_2O)					
Regeneration Air Temperature					
Regeneration Air Flow Rate					
Exit Temperature ^{o}F					
Percent SO_2 Inlet					
Percent SO_2 Outlet					

Table 14

☐ Electrostatic Precipitator (ESP)

SECTION	1	2	3	4	PERFORM. TEST
Primary Current (Amps)					
Primary Voltage (Volts)					
Secondary Current (MA)					
Secondary Voltage (KV)					
Spark Rate (SPK/MIN)					
Vent Gas Flow, SCFM					

☐ High Efficiency Mist Eliminator

☐ High Velocity Mist Eliminator

☐ Dual Pad Mist Eliminator

SECTION	1	2	3	4	PERFORM. TEST

Additional Observations

Table 15

Records Summary

Comparison Parameters	Perform Test Values	Values Over Perform Test Date								Approx. Allow. Value

Typical Abatement Equipment Readings During Performance Test

Parameter	Unit 1	Unit 2	Unit 3	Unit 4	Average in Industry
Particulate Efficiency (%)					95+%
Scrubber Pressure Drop (in. H_2O)					60+
Scrubber Water Flow Rate $\frac{\text{gpm}}{\text{1000 scfm}}$					5 to 10
Precipitation Spark Rate, (spm)					50 to 400
Primary Voltage					20 to 100 kv
Primary Amps					1
Flow Rate, (scfm)					30,000 to 300,000
Inlet temp., (°F)					300°
Opacity or Ringlemann No.					0

Malfunctions

Date	Description	Max Monitor Reading	Repetitious Occurrences				

Table 16

ADDITIONAL OBSERVATIONS

General Plant Appearance ______________________

Equipment Needing Attention ______________________

Fugitive Emissions and Leaks ______________________

Table 16 (continued)

FURNACE INTERIOR – ACID SLUDGE INSPECTION CHECK

Furnace Pressure
☐ positive
☐ negative

Have operator open furnace door. Use extreme caution when looking into furnace. Wear either a face shield or safety glasses: Use proper filters to protect eyes against brightness of flame.

A. Furnace Walls

	Satisfactory	Unsatisfactory	Last Maintenance Date
Cracks and/or Leaks			
access doors	☐	☐	______
breechings	☐	☐	______
air ducts	☐	☐	______
Interior refractory	☐	☐	______
B. Sludge Fired Units			
Acid sludge storage tank cleaning frequency	☐	☐	______
Sludge preheat temperature °F	☐	☐	______
Atomization pressure psi	☐	☐	______
Burner maintenance frequency	☐	☐	______
C. Sulfur Fired Units			
Burner maintenance frequency	☐	☐	______
Flame Characteristics			
Impingement on walls and arches	☐	☐	
Flame pattern	☐	☐	

Characteristics related to air quantities (circle)

	Excess	Normal	Lack
Sprayer	White	Yellowish Orange	Grey
Burners	Totally Blue	Blue and Yellow Mix	Totally Yellow

CONTROL PANEL INSTRUMENTATION

	Satisfactory	Unsatisfactory	Last Maintenance Date
Secondary chamber temperature °F	☐	☐	______
Gages reading properly	☐	☐	______
Graph recording time trace	☐	☐	______

FANS AND DUCTWORK

	Satisfactory	Unsatisfactory	Last Maintenance Date
Fan condition	☐	☐	______
Duct condition	☐	☐	______

TABLE 17

FOLLOW-UP PROCEDURES AFTER INSPECTING SULFURIC ACID PLANT

Compliance Parameter	Course of Action
Visual emissions	If opacity is constantly over 10 percent, issue citation. If plant personnel have isolated the problem, inquire how long it will take to remedy the situation. Enforcement officer should request a compliance schedule in a follow-up letter.
Opacity, SO_2, SO_3 monitors	a. Not in operation - issue citation. b. Not properly calibrated or zeroed - advise plant personnel to implement a satisfactory program which might include services of outside consultants.
Control equipment	a. Not in operation - request in follow-up letter schedule to repair instruments. b. Values indicating unit out of compliance- Determine reasons - have plant take appropriate corrective action.
Records	a. Not kept - Issue citation. b. Values indicating plant is out of compliance: i. monitors - If SO_2 and/or SO_3 standards are exceeded more than 5 times a month for intervals less than 4 hours, issue citation. - If SO_2 and/or SO_3 standard is exceeded more than 8 continuous hours, issue citation. - If opacity standard is ever exceeded for more than 2 hours, issue citation. c. Daily instrument zero/calibration - Issue citation if instruments are not zeroed and calibrated within 3 or more consecutive days. d. Fuel analysis - Units without SO_2 control equipment must analyze fuel daily. e. Malfunction records - If complete information (time, levels, malfunction description, problem correction methods) is not recorded for all malfunctions, issue citation.

Table 18

PLANT LOG

Data Sheet 1 of 3

Sulfuric Acid Plant:

Unit:

Date:

Run Number

PARAMETER	PM TIME (MIN.)										
Water Content of Sulfur (wt. %)											
Hydrocarbon Content of Sulfur (wt. %)											
Gas Temperature to Converter (^{O}F)											
SO_2 Concentration to Converter (vol. %)											
Gas Temperature to Economizer (^{O}F)											
Gas Temperature to Absorber (^{O}F)											
Stack Gas Flow Rate											
Stack Gas Temperature (^{O}F)	See Test Results										
Stack Gas Pressure											
Acid Flow Rate to Absorber (gpm)											
Acid Temperature to Absorber (^{O}F)											
Acid Concentration to Absorber (wt. %)											
Acid Concentration to Drying Tower (wt. %)											
Acid Production Rate (Flowmeter)											
Gas Temperature from No. 1 Boiler (^{O}F)											

Production Rate = TPD 100% H_2SO_4

Table 18

Data Sheet 2 of 3

Sulfuric Acid Plant:

Unit:

Date:

Run Number:

PARAMETER	PM TIME (MIN.)										
Sulfur Feed Rate(% gauge)											
Air Flow Rate to Drying Tower (acfm)											
Air Temperature to Drying Tower (^oF)											
Air Pressure to Drying Tower (inches H_2O)											
Water Content of Air to Drying Tower											
Water Content of Air to Furnace											
Air Flow Rate to Furnace (acfm)											
Air Temperature to Furnace (^oF)											
Air Pressure to Furnace											
Gas Temperature from Furnace (^oF)											
O_2 Concentration to Converter (vol. %)											
Water Content of Gas to Converter											
Gas Temperature from First Stage (^oF)											
Gas Temperature to Second Stage (^oF)											
Gas Temperature from Second Stage (^oF)											
Gas Temperature to Third Stage (^oF)											

Data Sheet 3 of 3

Table 18

Sulfuric Acid Plant:

Unit:

Date:

Run Number:

PARAMETER	PM TIME (MIN.)										
Gas Temperature from Third Stage (^oF)											
Gas Temperature to Fourth Stage (^oF)											
SO_2 Concentration from Absorber (vol. %)											
O_2 Concentration from Absorber (vol. %)											
Acid Temperature from Absorber (^oF)											
Acid Concentration from Absorber (wt. %)											
Acid Flow Rate to Drying Tower (gpm)											
Acid Temperature to Drying Tower (^oF)											
Acid Temperature from Drying Tower (^oF)											
Acid Concentration from Drying Tower (wt. %)											
Gas Temperature from No. 2 Boiler (^oF)											
Conversion (%)											

Remarks: Started Run No. at p.m.; finished at p.m.

SECTION 8

BIBLIOGRAPHY

Waeser, B., *Handbuch der Schwefelsaurefabrikation*, Handbook for the Manufacture of Sulfuric Acid, Vols. 1 to 3, Braunschweig: Vieweg, 1930.

Waeser, B., *Die Schwefelsaurefabrikation*, The Manufacture of Sulfuric Acid, Braunschweig: Vieweg, 1961.

Kusnezow, D. A., *Die Herstellung der Schwefelsaure*, The Manufacture of Sulfuric Acid, Leipzig: Fachbuchverlag VEB, 1954.

Duecker, W. W. and J. R. West, *The Manufacture of Sulfuric Acid*, New York: Reinhold, 1959.

Fairlie: *Sulfuric Acid Manufacture*, New York: Reinhold, 1947.

Winnacker, K. and L. Kuchler: *Chemische Technologie*, Technology of Chemistry, Vol. 2, Inorganic Technology II, 2nd ed., Munchen: Hanser, 1959. pp. 18-70.

Ullmanns Encyklopadie der technischen Chemie, Ullmann's Encyclopedia of Technical Chemistry, Munich. Berlin: Urban and Schwarzenberg, 1962, Vol. 12, pp. 16, 21, 129; Vol. 13, p. 107; Vol. 15, pp. 424-465.

Gmelin, *Handbuch der anorganischen Chemie*, Handbook of Inorganic Chemistry, Syst. No. 9, see Part A, 1942 (reprint, 1952), pp. 286-484; Syst. No. 9, see Part B, 2nd ed., sulfuric oxy-acids, 1960, pp. 613-798.

Werth, H., *Dechema-Monographien*, Dechema-Monographies, Nos. 895 to 911, Vol. 52. Waste water- solid waster- waste gases, Weinheim: Verlag Chemie, 1964.

Amelin, A. G., *The Preparation of Sulfuric Acid from H_2S According to Wet Catalysis Methods*, (Russian), Moscow: Goskhimizdat, 1960.

REFERENCES

1. Calvin, E. L., F. D. Kodras. Evaluation of Emissions During Start-up, Shutdown and Malfunction of Sulfuric Acid Plants. Industrial Environmental Research Laboratory, EPA, by Catalytic, Inc., Charlotte, N.C. EPA-600/2-76-010. January 1976. 353 pp.

2. Farkas, M. D. and R. R. Dukes. Multiple Routes to Sulfuric Acid, CHEMICAL ENGINEERING PROGRESS, Vol. 64, No. 11, Nov. 1968, pp. 54-58.

3. Atmospheric Emissions from Sulfuric Acid Manufacturing Processes. Cooperative Study Project: Manufacturing Chemists' Association, Inc., and Public Health Service, U. S. DHEW, PHS. Division of Air Pollution. Cincinnati, Ohio, PHS. Publication No. 999-AP-13, 1965. 127 pp.

4. Chemical Construction Corporation. Engineering Analysis of Emissions Control Technology for Sulfuric Acid Manufacturing Processes. Final Report, Contract 22-69-81, Public Health Service, U.S. DHEW, PHS. National Air Pollution Control Administration, Publication No. PB-190-393. March 1970, Vols. I and II.

5. Moller, W., and K. Winkler. The Double Contact Process for Sulfuric Acid Production, presented at 60th Annual Meeting APCA, Cleveland, Ohio. June 1967, J.A.P.C.A., Vol. 18, No. 5. pp. 324-325.

6. Control Techniques for Sulfur Oxide Air Pollutants, National Air Pollution Control Administration, Washington, D.C., Publication No. AP-52, January 1969, pp. 3, 4, and 81.

7. Tucker, W. G.,APCO, Seattle, Washington and J. R. Burleigh, Chemical Construction Corp. SO_2 Emission Control from Acid Plants. CHEMICAL ENGINEERING PROGRESS, Vol. 67, No. 5. pp. 57-63.

8. York, O.H. and E. W. Poppele. Two-Stage Mist Eliminators for Sulfuric Acid Plants. CHEMICAL ENGINEERING PROGRESS. 60: 67-72, November 1970.

9. Brink, J. R., Jr., W. F. Burggrabe, and L. E. Greenwell. Mist Eliminators for Sulfuric Acid Plants. CHEMICAL ENGINEERING PROGRESS. 64: 85, November 1968.

10. Sulfuric Acid Process Reduces Pollution. CHEMIST ENGINEERING NEWS, 42(40): 42-43, December 21, 1964.

REFERENCES

11. Lawler, C. Air Pollution Control by a Sulfur Dioxide Scrubbing System. Presented at Semiannual Technical Conference of APCA, Houston, Texas. December 1967.

12. Donovan, J. R. and P. J. Stuber. The Technology and Economics of Interpass Absorption Sulfuric Acid Plants. American Institute of Chemical Engineers, New York, New York. Presented at the AIChE Meeting, Los Angeles, California. December 1-5, 1968.

13. Guidelines for Limitation of Contact Sulfuric Acid Plant Emissions. EPA Publication No. APTD-0602 and No. APTD-0711.

14. Burkhardt, D. B. Kinetic Plots Air Catalytic Operations. CHEMICAL ENGINEERING, June 26, 1961. pp. 115-116.

15. Burkhardt, D. B. Increasing Conversion Efficiency. CHEMICAL ENGINEERING PROCESS, Vol. 64 No. 11, November 1968. pp. 66-70.

16. Pedroso, R.I. Davy Powergas Inc. Lakeland, Florida. An update of the Wellman-Lord Flue Gas Desulfurization Process. EPA-600/2-76-136, May 1976. pp. 719-733.

17. Ennis, C. E. APCI/IFP Regenerative FGD Ammonio Scrubbing Process. EPA-600-2-76-136b, May 1976. pp. 865-875.

18. SO_2-Recovery from Sulphuric Acid Plant Off-Gases. Sulfur, No. 80. pp. 36-38.

19. Jimeson, R. M. and R. R. Maddocks. Sulfur Compound Cleanup: Trade-offs in Selecting SO_x Emission Controls. CHEMICAL ENGINEERING PROGRESS, August 1976. pp. 80-88.

20. Kiovsky, J. R., P. B. Koradio, and D. S. Hook. Molecular Sieves for SO_2 Removal. CHEMICAL ENGINEERING PROGRESS, August 1976. pp. 98-103.

21. Stasney, E. P. Electrostatic Precipitation. CHEMICAL ENGINEERING PROGRESS. 62:48, April 1966.

22. Shah, I. S. Acid Mist Recovery and Control. CHEMICAL ENGINEERING PROGRESS, Vol. 67, No. 5, May 1971. pp. 50-56.

REFERENCES

23. Remires, Raul. Double-Absorption Gets U. S. Foothold. CHEMICAL ENGINEERING, January 27, 1969. pp. 80-82.

24. Kamimura, Yoshihiko. Double Contact Process for Sulfuric Acid Manufacturing Facility, Ryusan (J. Sulfuric Acid Association, Japan), 20:167-177, 1967.

25. SO_2 Scrubber - Two Scrubbers Better Than One, CHEMICAL ENGINEERING, New York, New York, 62: 132-134, February 1955.

26. Emission Testing Compliance Manual, PEDCo-Environmental Specialists, Inc., EPA Contract No. 68-02-0237, Task No. 19, August 1974.

27. Standards of Performance for New Stationary Sources, Supplemental Statement in Connection with Final Promulgation, FEDERAL REGISTER, Vol. 37, No. 55-Tuesday, March 21, 1972.

28. Calvin, E. L., F. D. Kodras. Effect of Equipment Maintenance and Age on Sulfuric Acid Plant Emissions. Industrial Environmental Research Laboratory, EPA, by Catalytic, Inc., Charlotte, N.C. EPA-600/2-76-119, April 1976. pp. 93.

APPENDIX A

STANDARDS OF PERFORMANCE FOR NEW STATIONARY SOURCES
CODE OF FEDERAL REGULATIONS

NSPS STANDARDS AND PERFORMANCE TEST METHODS

Federal Register (NSPS)
December 23, 1971
May 2, 1973
October 15, 1973

PERFORMANCE TEST METHODS

Method 1: Sample and Velocity Traverse

Method 2: Determination of Velocity and Volumetric Flow Rate

Method 3: Gas Analysis

Method 4: Determination of Moisture in Stack Gas

Method 7: Determination of No_X

Method 8: Determination of SO_2

Method 9: Visual Opacity Determination

Method 1

1. Stack height and diameter.
2. Location of sample port.
3. Location of traverse points.

Method 2

1. Stack static pressure.
2. Obtain Pitot tube coefficient.
3. Stack temperature.
4. Average traverse and temperature.
5. Barometric pressure at plant site.

Method 3

1. Gas Analysis

Method 4

1. Average stack temperature.
2. Moisture train data, meter temperature, rotameter setting, meter readings and clock time.
3. Water volume increase.
4. Barometric pressure at plant site.

Method 7

This test is done in an analytical laboratory and the sample collection technique is all that can be checked at the plant site. The test result must be obtained from the analytical laboratory. The identification of the analytical laboratory should be obtained and a check made of its reputation.

TEST REPORT FORMAT

Process Sections

- I. Table of Contents
- II. Introduction
- III. Summary and Discussion of Results
- IV. Process Description and Operation
- V. Sampling and Analytical Procedures
  - a. Location of Sampling Point
  - b. Analytical Procedures

Appendix

- A. Complete Particulate Results with Example Calculations
- B. Complete Gaseous Results with Example Calculations
- C. Complete Operation Results (with Example Calculations)
- D. Field Data
- E. Operating Data Log
- F. Sampling Procedure
- G. Laboratory Report
- H. Test Log
- I. Project Participants
- J. Correspondence with Source

Performance Test

Process Operating Conditions

During the performance tests as required by the NSPS, the sulfuric acid plant must be operated under these conditions:

1. The plant must be operated at or above its design production rate. The acid concentration must be at or above the design concentration.

2. The plant must be operated under the same conditions as planned for future operation.

3. The emission is expected to be at or under four pounds of sulfur oxides as sulfur dioxide per ton of sulfuric acid produced (100% basis).

Process Observation

The total time involved for a performance test is two hours. This includes four samples (Method 9) at one-quarter hour intervals. Additional time is required to select the sampling point in the stack and determine the volumetric flow rate. During the two-hour period the plant must be operated at a constant production rate, and the acid concentration should remain essentially constant. Process observations of the plant operation should be tabulated in log form during this test period. An example log form for these observations is presented in Tables 17.2 to 17.4. The following minimum observations should be logged:

Flow Rates

1. Air to Converter
2. Air to Furnace
3. SO_2 to Converter
4. Absorption Water to Absorber
5. Acid Production
6. Cooling Water to Absorber
7. Flow Ratio of Oxygen to SO_2- Air Mixture (flow to each converter bed)
8. Fuel Gas to Abater System (if applicable)

Temperatures

1. Air from Compressor
2. Oxygen Vapor to SO_2 - Air Mixture
3. Reaction Gases from Converter
4. Process Gas to the Absorber
5. Tail Gas from the Absorber
6. Tail Gas to the Abater System
7. Tail Gas from the Abater System
8. Absorption Water to Absorber
9. Product Acid from the Absorber
10. Cooling Water to the Absorber
11. Cooling Water from the Absorber

Pressures

1. Air Compressor Discharge
2. Oxygen Vapor to SO_2 - Air Mixture
3. Reaction Gases from the Converter
4. Process Gas to the Absorber
5. Tail Gas from the Absorber
6. Tail Gas to the Abater System
7. Tail Gas to the Expander

Analysis

1. Product Acid Concentration
2. Tail Gas to the Abater System
3. Tail Gas from the Abater System
4. Sulfur Dioxide Concentration in the Stack Gas (continuous, required by NSPS)
5. Stack Opacity
6. Any other process gas analysis made by operators in plant operation (these should be logged and identified).

Remarks

A column should be provided to record any unusual events that affect the plant operation and/or tests. Also check regular plant log remarks. By having the log form prepared before the performance test and recording the above observations at fifteen-minute intervals an operating picture is obtained. This log will verify the operation as submitted in a permit application or review of plans submitted to the EPA Administrator.

APPENDIX B

VISIBLE EMISSION OBSERVATION FORM

APPENDIX B

Date ____________________ Plant name ________________________________

Observer____________________ Plant address ________________________________

Observation Point________________

Stack - Distance* ____Height____

Wind - Speed______Direction______

Sky condition: ________________

Color of emission: ____________

Fuel____________________

Observation began______Ended______

Comments: ________________

Observer's Signature________________

Remarks: ________________

sec min	0	15	30	45	sec min	0	15	30	45
0					30				
1					31				
2					32				
3					33				
4					34				
5					35				
6					36				
7					37				
8					38				
9					39				
10					40				
11					41				
12					42				
13					43				
14					44				
15					45				
16					46				
17					47				
18					48				
19					49				
20					50				
21					51				
22					52				
23					53				
24					54				
25					55				
26					56				
27					57				
28					58				
29					59				

*Distance from observer to stack.

APPENDIX B

RECORD OF VISUAL DETERMINATION OF OPACITY

PAGE___of___

COMPANY____________________
LOCATION____________________
TEST NUMBER____________________
DATE____________________
TYPE FACILITY____________________
CONTROL DEVICE____________________

HOURS OF OBSERVATION____________________
OBSERVER____________________
OBSERVER CERTIFICATION DATE____________________
OBSERVER AFFILIATION____________________
POINT OF EMISSIONS____________________
HEIGHT OF DISCHARGE POINT____________________

CLOCK TIME	Initial			Final
OBSERVER LOCATION Distance to Discharge				
Direction from Discharge				
Height of Observation Point				
BACKGROUND DESCRIPTION				
WEATHER CONDITIONS Wind Direction				
Wind Speed				
Ambient Temperature				
SKY CONDITIONS (clear, overcast, % clouds, etc.)				
PLUME DESCRIPTION Color				
Distance Visible				
OTHER INFORMATION				

SUMMARY OF AVERAGE OPACITY

Set Number	Time	Opacity	
	Start--End	Sum	Average

Readings ranged from ____ to ____ % opacity

The source was/was not in compliance with ____ at the time evaluation was made.

APPENDIX C

SUGGESTED CONTENTS OF STACK TEST REPORTS

CONTENTS OF STACK TEST REPORTS

In order to adequately assess the accuracy of any test report, the basic information listed in the following suggested outline is necessary:

1. Introduction - Background information pertinent to the test is presented in this section. This information shall include but not be limited to the following:

    a. Manufacturer's name and address.
    b. Name and address of testing organization.
    c. Names of persons present, dates and location of test.
    d. Schematic drawings of the process being tested showing emission points, sampling sites, and stack cross section with the sampling points labeled and dimensions indicated.

2. Summary - This section shall present a summary of test findings pertinent to the evaluation of the process with respect to the applicable emission standard. The information shall include, but not be limited to the following:

    a. A summary of emission rates found.
    b. Isokinetic sampling rates achieved if applicable.
    c. The operating level of the process while the tests were conducted.

3. Procedure - This section shall describe the procedures used and the operation of the sampling train and process during the tests. The information shall include, but not be limited to the following:

    a. A schematic drawing of the sampling devices used with each component designated and explained in a legend.
    b. A brief description of the method used to operate the sampling train and procedure used to recover samples.

4. Analytical Technique - This section shall contain a brief description of all analytical techniques used to determine the emissions from the source.

5. Data and Calculations - This section shall include all data collected and calculations. As a minimum, this section shall contain the following information:

   a. All field data collected.
   b. A log of process and sampling train operations.
   c. Laboratory data including blanks, tare weights, and results of analysis.
   d. All emission calculations.

6. Chain of Custody - A listing of the chain of custody of the emission test samples.

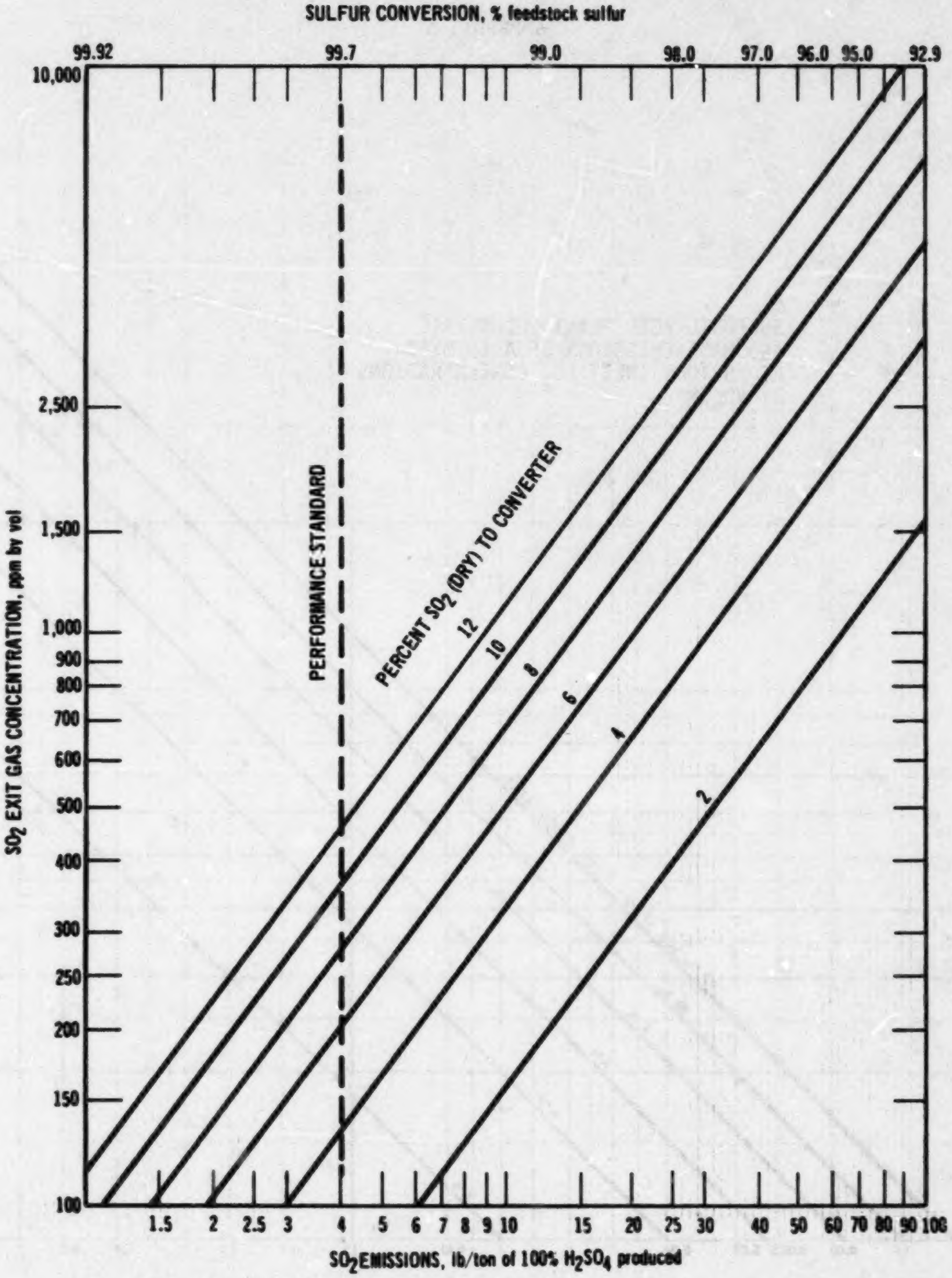
7. Appendix: (Within this Stack Test Report)

   a. Calibration work sheets for sampling equipment.
   b. Calibration or process logs of process parameters.

APPENDIX D

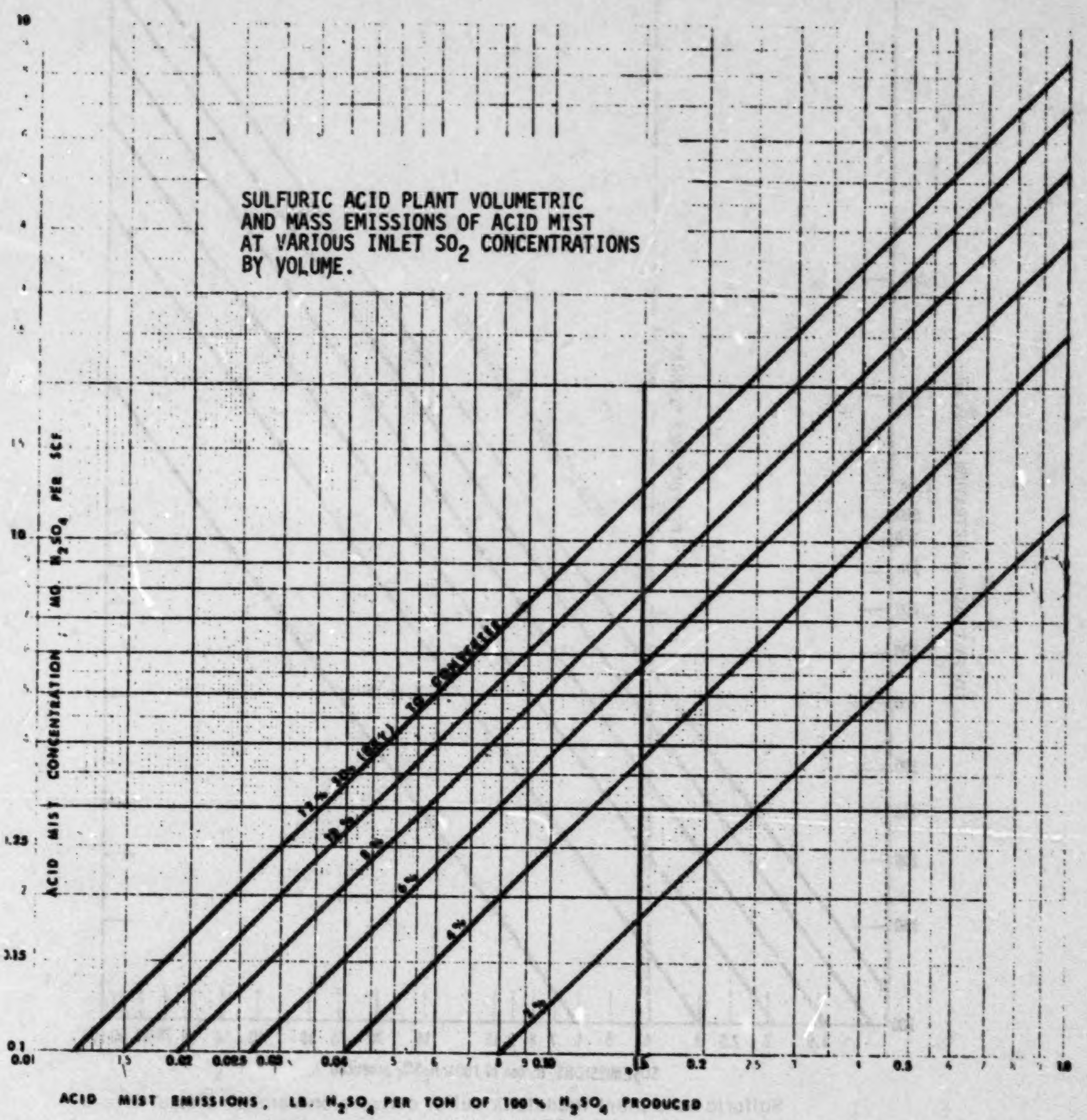
GAS CONVERSION GRAPHS

APPENDIX D



Sulfuric acid plant feedstock sulfur conversion versus volumetric and mass SO_2 emissions at various inlet SO_2 concentrations by volume.

APPENDIX D



SULFURIC ACID PLANT VOLUMETRIC AND MASS EMISSIONS OF ACID MIST AT VARIOUS INLET SO_2 CONCENTRATIONS BY VOLUME.

APPENDIX E

WATER POLLUTION FACTORS

Sulfuric Acid Plant Effluent Control

A sulfuric acid plant has no inherent water pollutants associated with the actual production of acid. An indispensable part of the process, however, is heat removal accomplished with steam generating equipment and cooling towers. These cooling methods require blowdown and subsequent disposal to natural drainage. The amount and degree of impurities discharged vary widely with the raw water quality.

An inherent hazard of any liquid handling process is the occurrence of an occasional accidental break and operator error. The sulfuric acid cooling coils are most prone to any accidental break. On these occasions the cooling tower water quickly becomes contaminated. In turn, the normally acceptable practice is to take care of that break as soon as it is discovered and protect the natural drainage waters.

Process Description

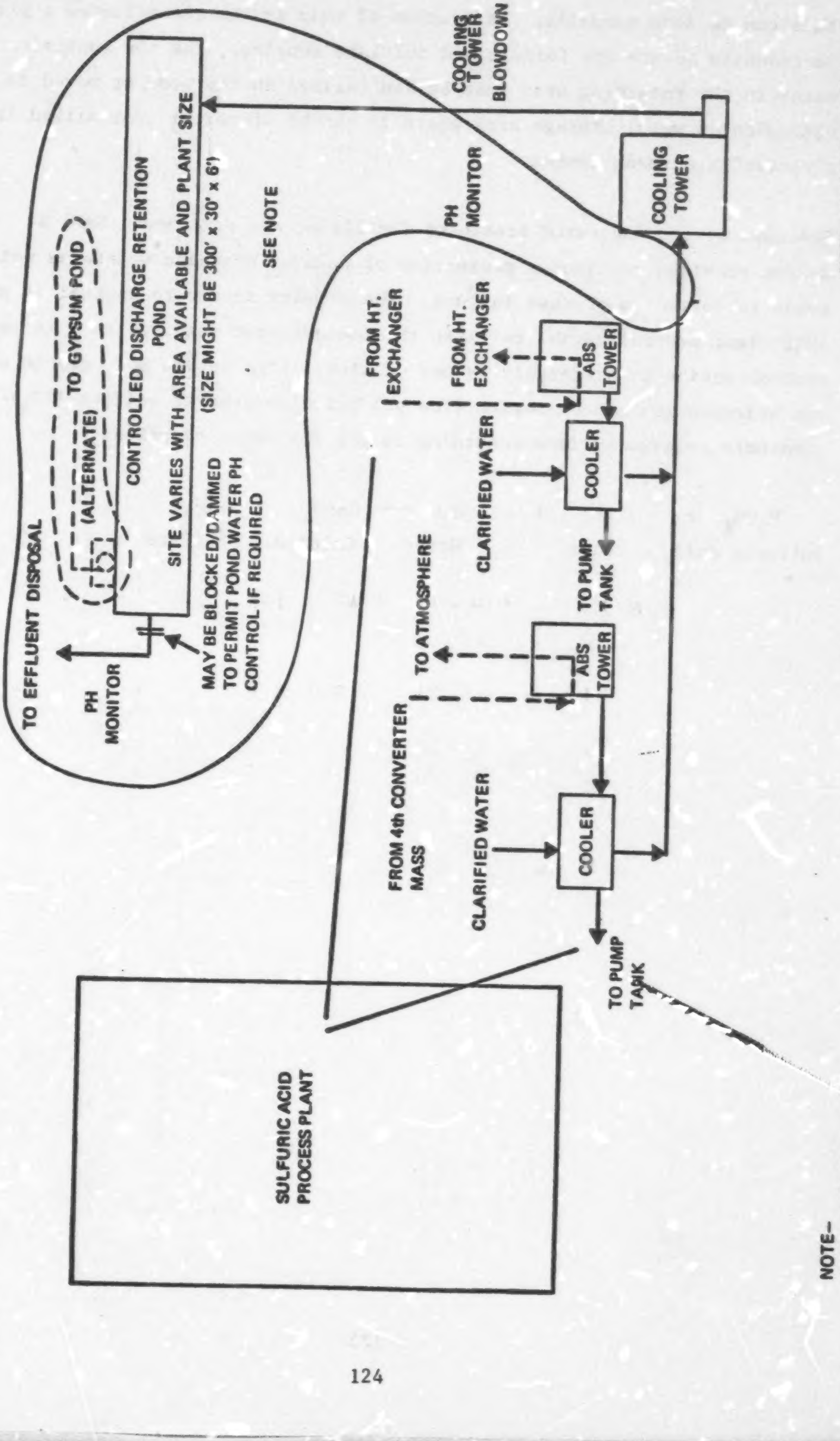
The facilities are relatively simple. These involve the installation of a reliable pH or conductivity continuous monitoring unit on the plant effluent stream (preferably, the combined plant effluent stream but at least on the cooling tower blowdown). A second part of the system is a retaining area through which noncontaminated effluent normally flows. This area can be any reasonable size but should be capable of retaining a minimum of 24 hours of the normal plant effluent stream. The discharge point from the retaining area requires a means of positive cutoff, preferably a concrete abutment fitted with a valve. A final part of the system is somewhat optional. For example, the retaining area could be provided with lime treatment facilities for neutralization. In addition, equipment for transferring this acid water from the retaining area to a contaminated water holding or recirculating system could also be provided.

The procedure is that an acid break is detected by the water monitoring instrument, located at the inlet of the cooling tower, and causes an audible alarm to be sounded. It is preferable to have the instrument automatically activate the positive cutoff at the discharge of the retaining area although this can be done manually. Activation of this system necessitates a plant shutdown to locate the failure and initiate repairs. The now contaminated water in the retaining area must be neutralized in the pond or moved to a contaminated water storage area where it can be stored or neutralized through a central treatment system.

Sketches of the suggested treatment facilities are attached. Such a system provides continuous protection of natural drainage waters as well as means to correct a process failure. The primary factor to control is pH. Sufficient neutralization to raise the contaminated water pH to 6 is required. Neutralization is preferably by use of lime. Lime serves not only to neutralize the hydrogen ion concentration (low pH) but also removes sulfate (SO_4) as an insoluble calcium sulfate according to the following reaction:

$$H_2SO_4 + CaO + H_2O \longrightarrow CaSO_4 \cdot 2H_2O$$

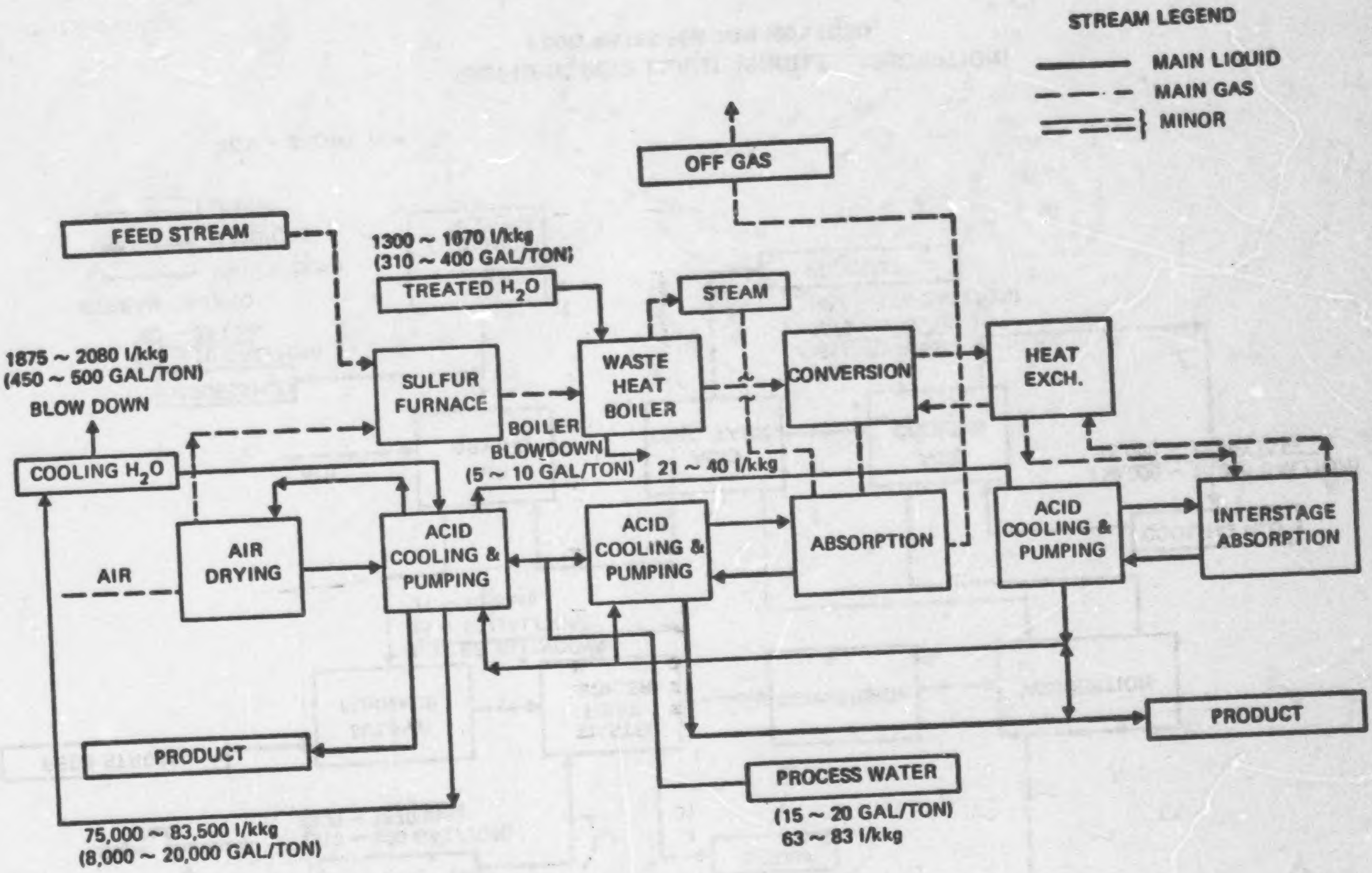
Sulfuric Acid Lime Water Calcium Sulfate


SULFURIC ACID PROCESS PLANT
FROM 4th CONVERTER MASS
CLARIFIED WATER
COOLER
TO PUMP TANK
ABS TOWER
FROM 4th CONVERTER
TO ATMOSPHERE
CLARIFIED WATER
COOLER
TO PUMP TANK
ABS TOWER
FROM HT. EXCHANGER
FROM HT. EXCHANGER
PH MONITOR
COOLING TOWER
COOLING T OWER BLOWDOWN
TO EFFLUENT DISPOSAL
PH MONITOR
MAY BE BLOCKED/DAMMED TO PERMIT POND WATER PH CONTROL IF REQUIRED
TO GYPSUM POND (ALTERNATE)
CONTROLLED DISCHARGE RETENTION POND
SITE VARIES WITH AREA AVAILABLE AND PLANT SIZE
(SIZE MIGHT BE 300' x 30' x 6')
SEE NOTE

NOTE–
CIRCLED ITEMS ADDED FOR EFFLUENT CONTROL

SULFURIC ACID EFFLUENT CONTROL

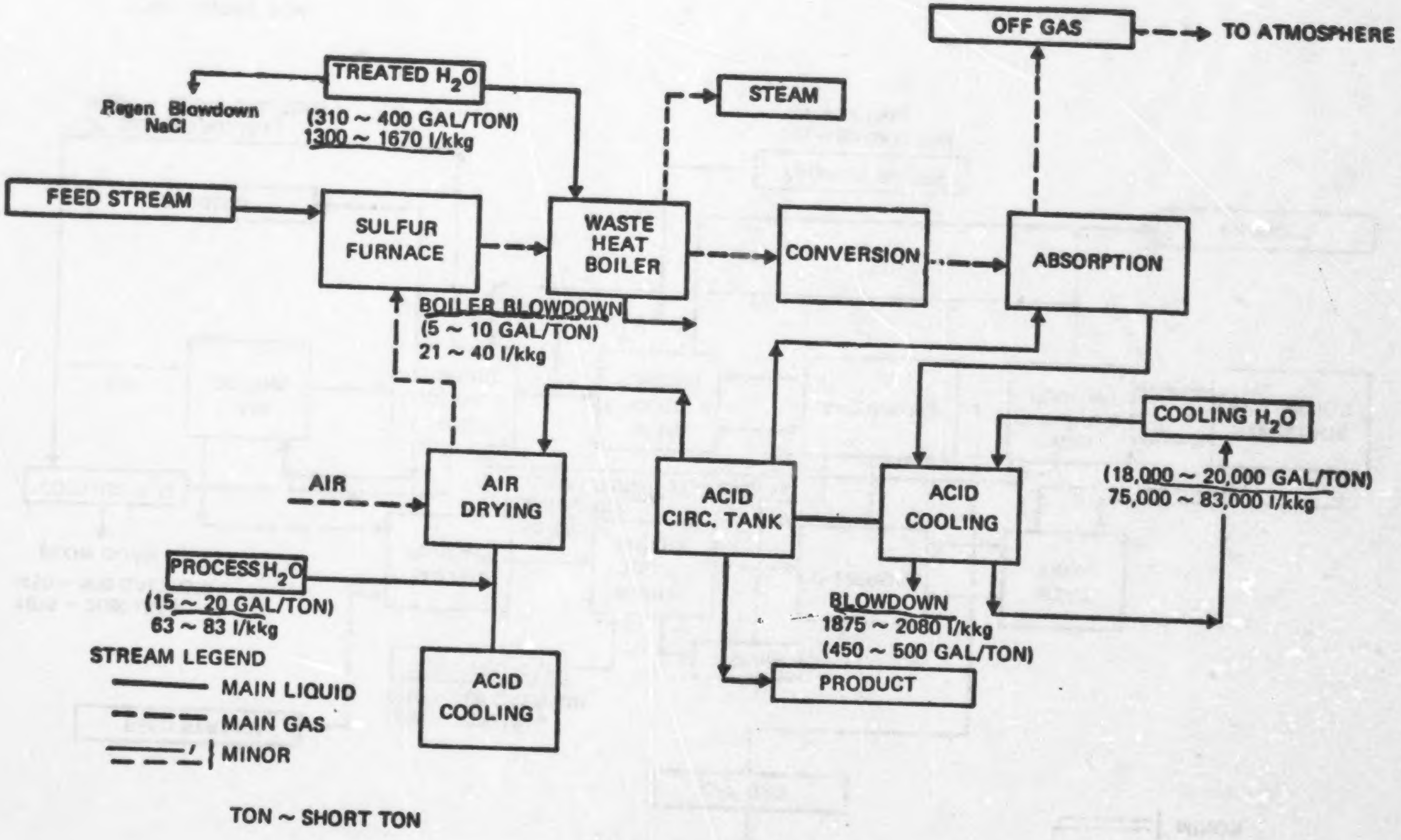
NOTE: THIS APPLIES TO BOTH SINGLE AND DOUBLE ABSORPTION PLANTS


STREAM LEGEND
MAIN LIQUID
MAIN GAS
MINOR
OFF GAS
FEED STREAM
1300 ~ 1670 l/kkg
(310 ~ 400 GAL/TON)
TREATED H_2O
STEAM
1875 ~ 2080 l/kkg
(450 ~ 500 GAL/TON)
BLOW DOWN
SULFUR FURNACE
WASTE HEAT BOILER
CONVERSION
HEAT EXCH.
BOILER BLOWDOWN
(5 ~ 10 GAL/TON)
21 ~ 40 l/kkg
COOLING H_2O
AIR
AIR DRYING
ACID COOLING & PUMPING
ACID COOLING & PUMPING
ABSORPTION
ACID COOLING & PUMPING
INTERSTAGE ABSORPTION
PRODUCT
PRODUCT
PROCESS WATER
(15 ~ 20 GAL/TON)
63 ~ 83 l/kkg
75,000 ~ 83,500 l/kkg
(8,000 ~ 20,000 GAL/TON)

TON ~ SHORT TON

SULFURIC ACID PLANT – DOUBLE ABSORPTION

FLOW RATES PER TON 100% H_2SO_4


OFF GAS
TO ATMOSPHERE
TREATED H_2O
Regen Blowdown
NaCl
(310 ~ 400 GAL/TON)
1300 ~ 1670 l/kkg
STEAM
FEED STREAM
SULFUR FURNACE
WASTE HEAT BOILER
CONVERSION
ABSORPTION
BOILER BLOWDOWN
(5 ~ 10 GAL/TON)
21 ~ 40 l/kkg
COOLING H_2O
(18,000 ~ 20,000 GAL/TON)
75,000 ~ 83,000 l/kkg
AIR
AIR DRYING
ACID CIRC. TANK
ACID COOLING
PROCESS H_2O
(15 ~ 20 GAL/TON)
63 ~ 83 l/kkg
BLOWDOWN
1875 ~ 2080 l/kkg
(450 ~ 500 GAL/TON)
PRODUCT
STREAM LEGEND
MAIN LIQUID
MAIN GAS
MINOR
ACID COOLING
TON ~ SHORT TON

SULFURIC ACID PLANT (SINGLE ABSORPTION)
FLOW RATES PER TON 100% H_2SO_4

APPENDIX F

SUMMARY OF TROUBLESHOOTING TECHNIQUES

A. High Opacity Stack Gas Plume by Moisture

1. Moisture in SO_2 gas or air.
2. Moist air leakage into ductwork system -- see next sections for corrective action.
3. Poor acid distribution over absorption or drying towers.
4. Insufficient flow rate of H_2SO_4, 98% acid circulating into towers.
5. Channeling due to dirty towers, absorption and drying.
6. Spray from drying tower.
7. Splashing at weirs.
8. Splash from leaking distributor tubes.
9. Leakage of internal acid piping.
10. Failure of plugging of entrainment separators.
11. Flooding of packing in the tower.
12. Sulfur impurities, oil, hydrocarbons, organic and excessive moisture form water by combustion due to the hydrogen content.

B. Mist Formed In System Between Converter Outlet and Absorbing Tower - Causing High Opacity Stack Gas Plume

13. Duct cooling below dewpoint - Refer to subsequent section corrective action.
14. Poor drying tower operation

    Entrained drying acid

    Inadequate gas purification

    Acidity of gas (SO_3)

    Organic matter in the sulfur

    Above conditions cause acid mist formation,
15. Absorbing tower operating conditions.
16. Acid strength too high (99.0-100%) + ($_2SO_4$) or acid too low (90-97.5% H_2SO_4).
17. Air leak at base of stack.
18. Temperature of gas entering absorption tower too high.
19. Insufficient acid flow rate - gpm.

20. Poor acid distribution.

21. Channeling due to dirty tower packing.

22. Tower packing settled, disarranged or disintegrated.

C. Sulfur Burning (Raw Gas) Units

23. Steam or water leaks. Sulfur line to burner. (Refer to subsequent pages for corrective action.

24. Leaks in the boiler, superheater, or economizer tubes.

25. Oxides of nitrogen in gas due to excessive combustion temperatures.

26. Quality of the sulfur or raw material.

27. Hydrocarbons or organics in sulfur.

28. Acidity in sulfur.

APPENDIX F

INSPECTION CHECKLIST FOR TROUBLESHOOTING MALFUNCTIONS, UPSETS AND POOR PROCESS OPERATOR CONTROL

All Types of Units, Including Equipment from Drying Tower to Exit Stack

SYMPTOM	CAUSE - Item Number	METHOD OF DETERMINATION (Verification Tests)	REMEDY
A. Excess Moisture in SO_2 gas or air			
	1. Poor drying	Make moisture tests of air or gas leaving the drying tower. Opacity is high.	Increase Acid Flow Rate.
	2. Moist air leakage	When the blower is located after the drying tower, make moisture test on air or gas in the blower discharge duct. (Atmospheric moisture may be drawn in the suction duct or connections of the blower.) Plume opacity is highly visible.	Locate leak and weld hole shut with patch of steel plate.
	3. Poor acid distribution. Dirty distributor or tubes. Distribution points too far apart or acid not equally distributed in the area and not level.	Inspect visually with and without acid circulating. Distributing points not more than 18-inch centers, no more than 12 inches from the inside of shell lining. Opacity reading is high.	Adjust distribution level position.
	4. Insufficient acid circulating in the towers.	Measure acid level in pans with a rod. Make sure pans are level. Check amperage of pump motors. Compare temperature of gas or air leaving the drying tower with temperature of the acid entering the tower. They should be approximately the same. Check the increase in acid temperature across tower. Opacity reading should be high.	Increase flow rate of acid.
	5. Channeling due to dirty tower.	Determine pressure drop through the tower, including and excluding the spray catcher. Inspect visually for sulfate on the top of tower packing. Wash tower if necessary.	Clean out tower packing and/or repack tower.

SYMPTOM	**CAUSE - Item Number**	**METHOD OF DETERMINATION** (Verification Tests)	**REMEDY**
B. Spray from drying tower	6. Exit Stack Plume greyish white.	Make stick test at exit duct. Two sticks at right angles to each other, and across the duct diameter, are necessary at times if flow pattern of gas including mist is distorted. Opacity reading is high.	Add new mist eliminator to top of tower.
	7. Splashing at weirs if the distributor is the weir type.	Examine visually with and without acid flowing. None of the weir streams should have any free drop from the bottom of the slots to the packing. Packing must come up to the bottom of each slot and should not splash at any weir.	Adjust distributors to no free drop.
	8. Splash from leaking distributor tubes.	Examine visually with acid circulation both on and off. Look for wet tubes.	Align piping.
	9. Leakage of internal acid piping.	Examine visually for leaks in internal acid pipe while acid is circulating at full normal rate.	Replace corroded pipe.
	10. Failure or plugging of entrainment separators.	Inspect. Measure pressure drop.	Wash or repack spray catcher if necessary.
	11. Flooding of packing in the tower or flooding of packing at the acid distributor due to improper packing, high acid or gas flow, or breakdown of packing.	Flooding evidenced by high pressure differential. Visual inspection of tower internals will show uneven distribution of packing or "washing" effect causing packing to move and relocate in an uneven manner.	Repack tower.

SYMPTOM	CAUSE - Item Number	METHOD OF DETERMINATION (Verification Test)	REMEDY
C. Mist formed in system between converter outlet and absorbing tower. High plume opacity readings indicated.			
	12. Cooling in SO_3 cooler or economizer is too great, too fast, or localized. Inadequate heat exchanger capacity.	Appearance of drip acid in the economizer or a larger-than-normal amount of drip acid drained from the SO3 cooler shell. This condition may be aggravated by an abnormally high mist content in the SO_3 gas. Opacity reading is high.	Improve control by operator and temperature control adjustments.
	13. Duct cooling.	Note if the poor appearance of the stack varies with atmospheric conditions. If appearance is worse during rainstorms, or during sudden changes in temperature and wind velocity, top shielding from rain or side shielding from wind may be required.	More insulation is required or better shielding provided.
	14. When large amounts of moisture are in the SO_3 gas leaving the converter, as from poor drying, entrained drying acid, inadequate gas purification, acidity or organic matter in the sulfur, etc., it is impossible to prevent acid mist formation. Much of the mist so formed cannot be removed in the absorbing tower and escapes as visible mist from the exit stack.	Can be detected quantitatively by mist tests of the gas entering and leaving the absorbing tower. Tyndall beam tests can be made on the gas leaving the equipment being tested. Sight glasses directly across the diameter of the absorbing tower, above the packing are helpful in determining whether the escape of fumes from the absorbing tower stack is due to unabsorbed SO_3 or sulfuric acid mist. The presence of mist in the gas will cause a cloudy appearance inside the tower. If the gas is clear inside the tower and the stack if fuming, the poor appearance of the stack is due to poor SO_3 absorption and not to mist in the gas.	Trace out entire plant for various equipment malfunctions and correct offender.

SYMPTOM	CAUSE - Item Number	METHOD OF DETERMINATION (Verification Tests)	REMEDY
D. Absorbing tower operating conditions.			
	15. Temperature of acid in the tower may be too high or too low.	Low acid temperature has more affect on stack than high temperature. Usually the minimum is 50°C (122°F) and and the maximum is 90°C (194°F) for acid entering.	The optimum temperature must be found by operating experience. Lower temperatures are generally permitted with better quality gas that contains less H_2SO_4 mist or vapor. If stack appearance is poor due to mist or moisture condition, it can usually be improved by increasing the temperture of the acid going to the tower to 90°C to 110°C. This is done only as a temporary measure to confirm that a mist or moisture condition exits.
	16. Acid strength too high or too low.	Determine optimum strength by actual operation, adjusting slowly within the range of 98.5 percent to 99.4 percent. Approximately 99.2 percent is good practice.	Same as above.
	17. Air leak at base of stack.	Visual inspection	Weld leaks tight.

SYMPTOM	CAUSE - Item Number	METHOD OF DETERMINATION (Verification Tests)	REMEDY
	18. Temperature of gas entering tower.	In plants that do not produce oleum, temperatures, of 150° to 160°C entering the absorber are low enough.	Temperatures could be considerably higher with good stack appearance, but with higher gas inlet temperature the absorbing acid temperature must be higher also and corrosion will be greater.
	19. Insufficient Acid Flow Rate	Check pump motor amperage check tower drain sight glass for flow.	Increase flow rate by proper valving or repair pump.
	20. Poor Acid Distribution	Same as Items 3 and 4 above in Verification Tests column.	Same as Item 3 and 4 in above Remedy column.
	21. Channeling due to dirty tower.	Determine pressure drop through the tower, both including and excluding the spray catcher. Inspect visually for sulfate on the top of tower packing.	Wash tower if necessary. Check Remedy, Item 5.
	22. Tower packing settled or disarranged.	When all other points have been checked and found satisfactory, this item might be the cause.	Packing under the distributor tubes may have to be removed and rearranged

SYMPTOM	CAUSE - Item Number	METHOD OF DETERMINATION (Verification Tests)	REMEDY
E. Sulfur Burning (Raw Gas) Units, Steam or Water Leaks.	23. Sulfur line to burner.	Disconnect line at burner with pump down and steam on jacket. Blanking at pump may be necessary. At times it may be possible to cut steam off the steam jackets carefully; stack will clear rapidly if a steam leak is the source of trouble. Do not allow sulfur in line to freeze.	Repair or replace leaky piping.
	24. Leaks in the boiler, superheater, or economizer tube.	Symptoms are a considerable increase in the condensed acid drip in SO_3 cooler and in the economizer or decrease in the amount of water required for dilution. Apply hydrostatic tests on boiler system equipment when leaks are suspected and cannot be detected. Comparative Tyndall beam tests can be made on gas entering and leaving equipment suspected of leaks.	Weld leaky tubes or plug. When boiler leaks are suspected, shut down and examine by inspection for water dropping from boilers into the compartments or ducts under the boiler or economizer. If leaks are very large, water will run out of drain nozzles under the boiler or economizer when blind flange is removed from the end of the drains.

SYMPTOM	CAUSE - Item Number	METHOD OF DETERMINATION (Verification Tests)	REMEDY
F. Oxides of nitrogen in gas.	25. Very high burner temperature causes nitrogen to combine with oxygen and form oxides of nitrogen, which tend to form sulfuric acid mist in the equipment between the converter and the absorbing tower.	Examine condensed drip in economizer or SO_3 cooler for niter. When drip is diluted with water, brown fumes will be noted if a considerable amount of niter is present.	Niter in the burner gas may be prevented by reducing the burner temperature, lowering SO gas strength, or lessening preheating of the air. This condition may be due to high localized temperatures that are not recorded or evident; it might be corrected by improving the sulfur spray distribution and burning pattern.
G. Quality of the sulfur or raw material		Laboratory analysis of the raw material is required.	
	26. Nitrogen compounds.	May occur in any of the raw materials, i.e., sulfur, H_2S or dilution acid (if unit uses spent acid in the tower acid circulating systems).	Use highest purity sulfur economically possible. Use lower sulfur flame temperature.
	27. Hydrocarbon or organics in sulfur.	Good sulfur filtering sometimes helps by partially reducing organics.	Use sulfuric acid in sulfur pit to coagulate hydrocarbons, then neutralize with lime and filter.
	28. Acidity in sulfur.	Neutralize acidity with lime, but only when sulfur is subsequently filtered.	Use highest purity sulfur economically possible or use liming and filtration of molten sulfur.